# Field Measurements and Source Analysis of Airborne Particulate Matter in London

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*Awarding institution:*
King's College London

# Field Measurements and Source Analysis of Airborne Particulate Matter in London, 2001 – 2012

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# Abstract

Datasets of PM10 measured gravimetrically and its key components from different locations (background, suburban, roadside, kerbside) in London during the period 2001 to 2012 have been collected and analysed. During this period a number of regulatory requirements and other initiatives, including a Low Emission Zone, were introduced targeting the reduction of PM10 because of its known adverse health effects. Analysis across the whole timescale was confounded by a change of filter substrate in 2007 but no evidence of any noticeable reduction in overall PM10 concentrations was found at the study sites. The contribution of the coarse fraction increased at Marylebone Road suggesting that road abrasion and brake and tyre wear from traffic sources became increasingly important. Pollution episodes, when PM10 concentrations exceeded 50 μg $m^{-3}$, were particularly noticeable in springtime and associated with increased ammonium nitrate concentrations. Ammonium sulphate concentrations reduced by approximately 30% at the time of the introduction of ultra-low sulphur fuel in the UK in 2007 signifying the importance of local sources of sulphate to PM10 concentrations. A high concentration (6.5 μg $m^{-3}$) of chloride in the fine fraction of PM10 at one of the sites in early November suggests that not all chloride concentrations may be associated with sea-salt and that anthropogenic chloride can make a significant contribution to pollution episodes.

Particulate black carbon from vehicle emissions has independently been linked to adverse health outcomes. The use of transmissometry and reflectometry to measure and compare the light absorbing properties of equivalent black carbon concentrations (EBC) on archived filters of different substrates was investigated. Equations for calculating daily EBC concentrations were determined and may be used at locations where measurements would not otherwise be available. A decrease in the region of 7% in overall mean EBC concentrations was detected at Marylebone Road after 2010. However, daily concentrations at all locations did not change in line with PM10 concentrations indicating a need for a separate long term monitoring programme of ambient EBC concentrations to track the results of exhaust abatement technologies and policies.

# Acknowledgements

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Thanks to everyone at the Environmental Research Group and Lung Biology Unit at King's College, London who made my return to studying so much easier. Particular thanks go to Dr Gary Fuller who has enthusiastically supervised the completion of this thesis, despite his extraordinarily busy schedule. Also special thanks to Dr Anja Tremper for all her help and insightful comments and Dr David Green for patiently answering all my queries and supplying me with relevant information.

This research has drawn on a large amount of data which have been the result of fieldwork and laboratory investigations carried out by many different individuals. I know from experience how time consuming, and on occasions frustrating, this can be, so their efforts are very much appreciated.

I have been very lucky to have had enormous support from my husband, Clive and son, Drew. Thank you for your patience (and cups of tea), particularly in the final few months of the project. I am sorry that my mother is no longer with us to see its completion. She was there at the start and enjoyed keeping Drew company when I was working. I hope she would have been proud of me and her grandson, now just starting his own postgraduate studies.

Finally, I would like to dedicate this thesis to the memory of Billy Kang who helped me enormously in the laboratory when I was both an undergraduate and postgraduate student. He helped make the transition from office worker to researcher easier. Thank you Billy. I missed you on my return to KCL.

# Declaration

I, Pamela Margaret Davy declare that all the work submitted in this thesis is my own and that all references are cited accordingly,

Signed ……(Pamela Davy)…….. (student)

Date ……10 October 2014

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# Chapter 1

## Introduction

Throughout the last decade and beyond there has been a determined effort by regulatory authorities and others to improve air quality because of its links with poor health outcomes. This is particularly demonstrable in London where air pollution has been a longstanding problem.

Edward I in the thirteenth century and Elizabeth I in the 16th century both tried, unsuccessfully, to ban the burning of 'sea-coal' in London because of unpleasant odours and reduced visibility (Brimblecombe, 1987). On 24 January 1684 John Evelyn noted in his diary, during a particularly cold period in London when the river Thames had frozen, that in London the ascent of smoke was hindered by the 'excessive coldnesse' and the air was "so filled with fuliginous steam of the Sea-Coale" that "filling of the lungs with its gross particles exceedingly obstructed the breast, so as one could scarcely breathe." (Evelyn, 1684). ("fuliginous" meaning "sooty"). Airborne particulate matter from coal burning, both industrially and domestically, continued to be a problem in London until the middle of the 20th century. An infamous air pollution episode in London in December 1952 caused by 'smog' – a combination of smoke from coal burning and fog – caused an estimated additional 4000 deaths (Maynard, 2001). The introduction of Clean Air Acts between 1956 and 1993

sought to regulate air pollutants at source but a new and different problem began to emerge. Increases in the use of vehicles in the UK for commercial and personal use introduced small, less predictable, mobile sources of airborne particulate matter into the atmosphere which were also found to be implicated in poor health outcomes.

It became necessary to consider ways in which ambient air quality should be monitored and regulated. One of the main targeted pollutants is airborne particulate matter less than 10 microns in aerodynamic diameter known as PM10.

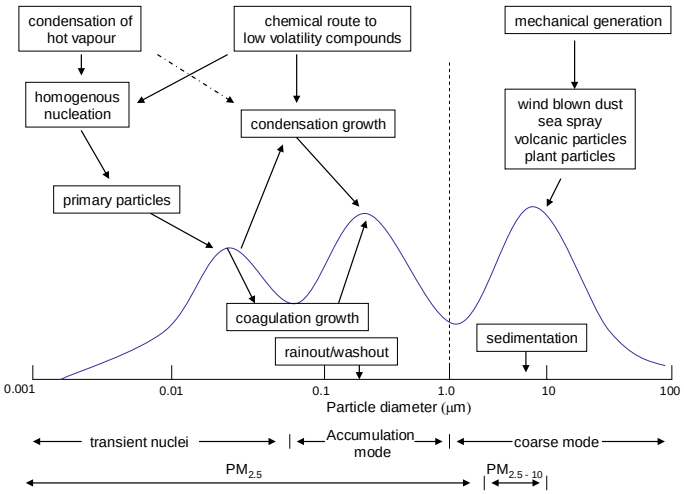
# Ambient PM10

Particles may be defined by their mass size, chemical composition, number concentration or optical properties. Mass size is one of the most common definitions but, because they are irregular in shape, the size of particles are commonly expressed in terms of their aerodynamic diameter which is defined as "the diameter of a sphere of unit density (1 g cm $^{-3}$) that has the same terminal falling speed in air as the particle under consideration" (Finlayson-Pitts and Pitts, 2000). Finlayson-Pitts and Pitts highlight the usefulness of utilising this term because the aerodynamic diameter of a particle determines its residence time in air and reflects the regions of the respiratory system where particles of different sizes may be deposited.

PM10 is a generic term recognised internationally describing any concentration of particles in the atmosphere where each particle has an aerodynamic diameter of less than 10 μm. 10 μm is generally thought to be the largest size of particle which may penetrate into the lung and circulatory system and hence potentially cause harm. The composition of PM10 varies in terms of type and size of particle which in turn varies depending on a number of factors including source (both from human activity and natural), meteorological circumstances, the interaction of different species once in the atmosphere. PM10 may also contain other specific regulated pollutants, such as lead, nickel and cadmium, within its composition.

Based on work carried out by Whitby et al. in 1972, $PM_{10}$ may be sub-divided into three distinguishable size ranges, see Figure 1.1. These have been found to differ substantially in composition, source and behaviour in the atmosphere.

*Figure 1.1 schematic diagram of the size distribution of airborne particles*




*(Source: based on Figure 2.1 AQEG (2005))*

Particles between 2.5 μm and 10 μm are commonly referred to as the coarse fraction (PMcoarse or $PM_{10-2.5}$) and the majority of elements found in this fraction are relatively inert chemically. Particles between 0.01 and 2.5 μm, are commonly referred to as the fine fraction ($PM_{2.5}$), and this size fraction typically includes the greatest number of particles. The fine fraction may be further sub-divided into two size fractions:

(1) particles between 0.08 and 1 – 2 μm are in the accumulation range and arise from the condensation of low-volatility vapours and coagulation of smaller particles; and

(2) particles between 0.01 and 0.08 μm are in the nucleation range and arise mainly from gas-to-particle conversion.

Whilst $PM_{10}$ is defined as the upper size limit, the lowest end of the size range is not defined – as Finlayson-Pitts and Pitts (2000) point out "there is no accepted criterion at which a cluster of molecules becomes a particle."

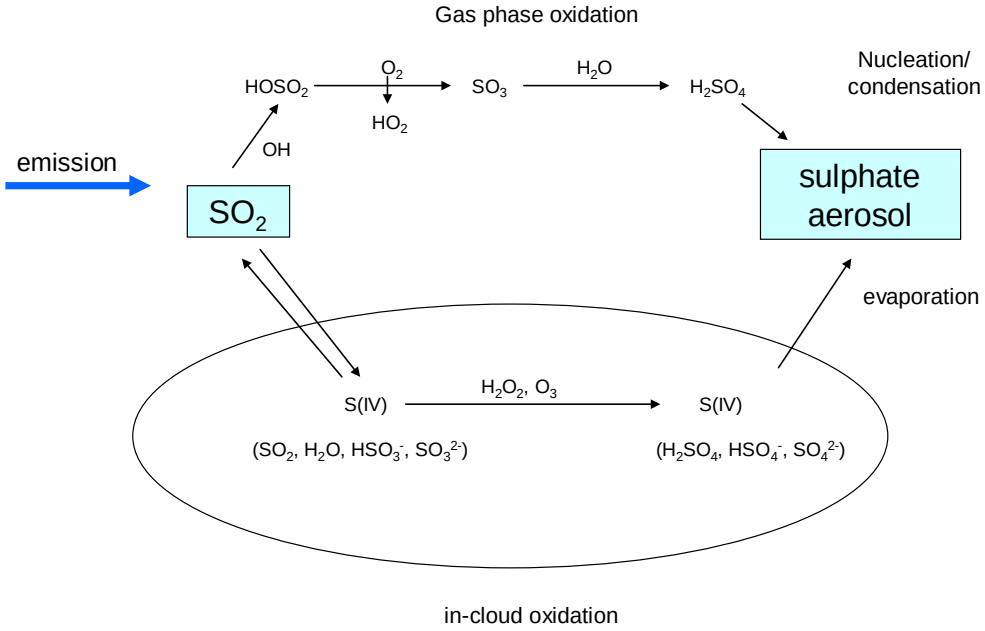
The major components of $PM_{10}$ are well documented (see QUARG (1996), APEG (1999), AQEG (2005), Heal et al. (2012)) and include sulphate, nitrate, ammonium, sodium, chloride, carbon (elemental and organic), mineral components (e.g. from rock or soil), metals, biological material (e.g. fungal spores, plant material) and water. The chemical composition of each particle depends, at least in the first instance, upon its source. Broadly there are two source categories: primary and secondary. Particles of each size fraction may occur from either source category.

Primary particles are directly emitted into the atmosphere and exist in the same form as those emissions. Where human activity is involved primary particles are produced from both stationary (e.g. industrial complexes, power stations) and mobile (e.g. road traffic) sources often as a result of incomplete combustion processes. Fresh emissions, varying from place to place, are constantly being introduced. In addition, particles from the mechanical break up of material such as tyres and brakes and road abrasion will be incorporated within this source category. Primary sources also include biological material such as plant and pollen fragments and other material, for example soil particles entrained by erosion or marine aerosols such as sodium chloride.

Secondary particles are not emitted directly. They are formed by chemical reactions in the atmosphere and then grow by coagulation with similar particles or with larger particles in the accumulation range. Secondary particles are mainly in the nucleation and accumulation ranges and contain more organic species than coarse particles (other than biological material) together with soluble inorganics such as sulphate ($SO_4^{2-}$), nitrate ($NO_3^-$), and chloride ($Cl^-$) and ammonium ($NH_4^+$). Precursors for secondary particles in the UK are thought to arise from the UK, Germany and/or France (APEG, 1999, Abdalmogith and Harrison, 2005).

The formation of **sulphate particles** generally arises from the photochemical oxidation of sulphur dioxide ($SO_2$) which is converted in the atmosphere to $SO_3$ and then combines with water vapour in the atmosphere to create sulphuric acid droplets ($H_2SO_4$). These droplets take up ammonia, $NH_3$, from the gas phase and are neutralised via ammonium bisulphate ($NH_4HSO_4$) to ammonium sulphate ($(NH_4)_2SO_4$). Oxidation may also occur in cloud droplets. Figure 1.2 gives an overview of these processes. The resulting particles are typically in the accumulation range, between 0.5 – 1.0 μm in size, and have a long atmospheric residence time making them available for long range transportation.

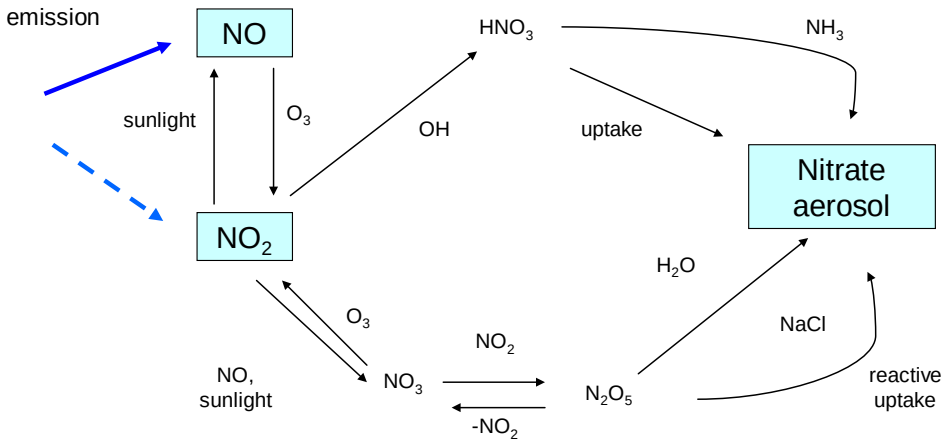
*Figure 1.2 Major chemical processes involved in sulphate aerosol production*




*Source Fig 4.3 AQEG, 2005*

Figure 1.3 shows the various routes by which **particulate nitrate** may be formed (AQEG, 2005). One of the main sources of particulate nitrate arises from the oxidation of NOx, which, in the UK, is emitted by vehicles and power stations. Gaseous nitric acid, $HNO_3$, is formed which is highly soluble and is scavenged by existing particles to form nitrate aerosol. Ammonium reacts with gaseous $HNO_3$ to form particulate ammonium nitrate ($NH_4NO_3$) in the fine fraction. Nitrate may also be generated via the formation of $N_2O_5$, generally at night time, which reacts with $H_2O$ on existing particle surfaces or aqueous droplets. Nitrate in the coarse fraction is present mainly as sodium nitrate formed by the reaction between gaseous nitric acid and sodium chloride.

*Figure 1.3 Major chemical processes involved in nitrate aerosol production*




Source *Fig 4.4 AQEG, 2005*

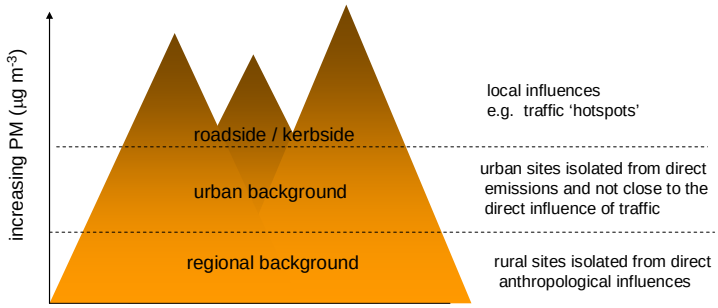
Emissions of ammonia ($NH_3$), an important component in the formation of both ammonium sulphate and ammonium nitrate in the fine fraction in ambient air, are mainly from agricultural sources, particularly livestock waste. Land management practices in the UK contribute 92% to total anthropogenic UK ammonia emissions (Misselbrook et al., 2011). There is an additional small contribution from three-way catalysts fitted to vehicles.

Particles are removed from the atmosphere either by coagulation, i.e. where two particles collide and adhere, which when it occurs with raindrops may lead to rain-out/washout, by sedimentation, or dry deposition. The latter process is size related with the larger particles settling more quickly. Particles are removed from the air at different rates in these processes. Maynard and Myers (2006) consider that, taking all days together, about 7% of 1 μm diameter particles and 15 – 30% of 3 – 5 μm are daily removed from the atmosphere. Generally speaking therefore the coarse fraction is likely to be more local in origin.

The nature, timing and quantity of emissions released to the atmosphere are infinitely variable depending on diverse choices and circumstances of industry, commercial activities and individuals. These emissions are then subject to external influences such as other particles/gases they encounter and meteorological/seasonal conditions. As Seinfeld (2004) points out the atmosphere "becomes a giant chemical reactor" once compounds are released into it.

Querol et al. (2004) analysed studies carried out between seven regions within the European Union (including two sites in the UK – London and Birmingham) and noted, using a methodology employed by Lenschow et al. (2001) illustrated by Figure 1.4, that PM concentrations increased from regional background sites through urban background sites to kerbside sites where the highest values were recorded. Lenschow et al. (2001) noted that in most studies $PM_{10}$ levels at kerbside sites are 30 – 50% higher than urban background sites. It was concluded that traffic (including exhaust and abrasion products) accounts for 35 – 55% of $PM_{10}$ at kerbside sites and 40 – 60% of $PM_{2.5}$.

*Figure 1.4 Schematic profile of ambient PM concentrations – based on Figure 5 Lenschow et al., 2001*



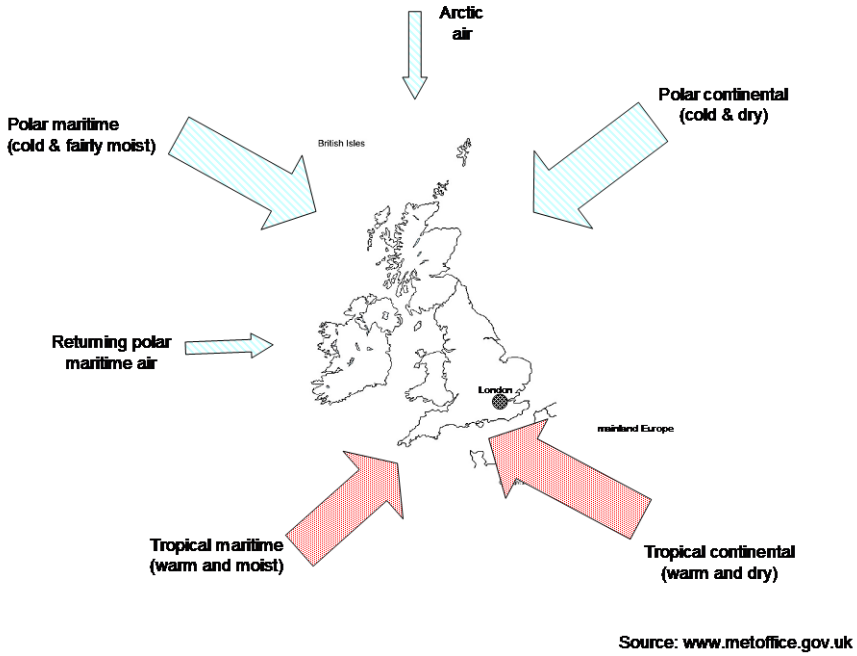

*Based on Figure 5, Lenschow et al (2001).*

# Climate influences

Day to day variation in PM is not simply a function of the varying amount of pollutants emitted. Meteorology, particularly in relation to the dispersion of pollutants, is important and is considered by Van Dingenen et al. (2004) to be the main factor controlling PM mass concentrations because as Mayes (1997) points out the mobility of the air is an important variable when determining air pollution. However, Elminir (2007) notes there is still little information on the dependence of the urban aerosol on, inter alia, meteorological conditions.

Daily variation in 'air mobility' is a common feature in the UK as the British Isles are at the crossroads of four main air masses – see Figure 1.5. Air masses travelling from the west over the Atlantic Ocean tend to be wetter than those which have travelled over the continent. Additionally air masses from the north are colder than those from the south. The boundary between two air masses is known as a front and it is common for the British Isles to be affected by a sequence of fronts, usually separating polar maritime and tropical maritime air masses. The warmer air rises above the cold denser air and the moisture condenses to form clouds and potentially rain. (www.metoffice.co.uk).

*Figure 1.5* *Diagram illustrating the principal air masses affecting the meteorology of the British Isles (www.metoffice.gove.uk)*




There has been much research which has sought to determine the provenance of pollutants by tracking the trajectory of air masses over the previous few days - see, for example, Smith et al. (2001), Buchanan et al. (2002) and Heal et al. (2005b). Highest nitrate and sulphate levels at sites in the UK were found by Abdalmogith and Harrison (2005) to be associated with air masses which had their origins in the near continent whilst highest chloride levels were associated with fast moving maritime trajectory categories. Smith et al. (2001) observed that $PM_{10}$ levels in London were influenced most by winds which originated from the south east and that wind speed was the next most important factor.

Wind speed is described by Kim et al. (2005) as a 'useful barometer' to distinguish the behaviour of different size fractions and they found that increased wind speed directly enhances the relative contribution of the coarse fraction in $PM_{10}$ mass concentration. In a study conducted in Cairo Elminir (2007) found that pollutants associated with traffic, including $PM_{10}$, were at their highest levels when wind speed was low. High PM

concentration episodes associated with meteorological situations during which there was reduced pollution dispersion were also observed by Putaud et al. (2004). Ruellan and Cachier (2001) noted that, whilst increasing wind speed had a dilution effect on concentrations of black carbon measured at a roadside site in Paris, wind speed did not seem to be an 'important driver for coarse particle concentrations'. On the other hand, Charron and Harrison (2005) found coarse particulate matter concentrations at Marylebone Road in central London increased when the wind speed increased and there was a 30% reduction of $PM_{2.5}$ from weaker to stronger winds.

$PM_{10}$ is also implicated in climate change processes because it has both light scattering and absorbing properties (AQEG, 2007). Climate change refers to variation in either the mean state of the climate or variability in the climate on a global scale over a long timescale and is commonly referred to when this variation is brought about by human activity. Climate change is however also an entirely natural process and the United Nations Framework Convention on Climate Change (UNFCCC) (unfccc.int) distinguishes between 'climate change' and 'climate variability', the latter being attributed to natural processes and the former to human induced change. In 2011 the Intergovernmental Panel on Climate Change (IPCC) (www.ipcc.) introduced a new definition that does not make this distinction. The UNFCCC convention is used here.

Climate change may affect air quality and, similarly, changes in air quality may affect climate change processes. For example secondary particulate matter, particularly sulphate, and its precursors scatter light and are thought to have an overall cooling effect whilst black carbon absorbs solar radiation and usually has a warming effect. In polluted clouds water droplet size reduces and droplet numbers increase. This reduction in droplet size inhibits the cloud's ability to form rain and therefore increases the duration of the cloud (cloud lifetime effect) (AQEG, 2007) It is unclear where the balance between these processes might lie although the IPCC (2007) considers that there is an overall cooling effect by anthropogenic contributions to aerosol.

AQEG (2007) in its report considering air quality and climate change in the UK acknowledge that changes in weather patterns are critical to air quality in the UK and discusses the effect changes in weather patterns might have. It considers that climate change will result in an impact on general weather patterns particularly 'wind climatology, temperature, sunshine hours and rainfall patterns.' It states that 'a potential decrease in the temperature differential between the Tropics and Polar Regions may result in an increase in areas of stagnant or stationary air masses.' It considers that in the UK stagnant periods in winter are unlikely to occur but periods of high pressure and stability are more likely to occur in hotter summers. The UK Climate Impacts Programme, 2009, (www.ukcip.org.uk) expects London's climate to change with less rainfall and a decrease in cloud cover in the summer (20 – 40% drier in the 2050s) and in the winter more rainfall (10 – 20% by the 2050s) with increasing mean wind speeds.

# Health effects

Studies in America, most notably the Harvard Six-Cities Study (Dockery et al., 1993) and the American Cancer Society Study (Pope et al., 1995), identified an association between air quality and poor health, including a risk of respiratory and cardiovascular problems. In the Six Cities Study $PM_{10}$, $PM_{2.5}$ and sulphate were found to be associated with daily mortality counts. These early studies were criticised for a number of reasons (see Vedal, 1997) but Pope and Dockery (2006) carried out a critical review of progress in this area of research since 1997 noting that these studies have been reanalysed and replicated with comparable associations being observed in other cities "with different climates, weather conditions, pollution mixes and demographics."

In 2010 the Committee on the Medical Effects of Air Pollutants (COMEAP) reported that the effect on mortality in 2008 in the UK due to anthropogenic particulate matter was equivalent to nearly 29,000 premature deaths. It also considered that air pollution alongside other factors may have made small contributions to the early deaths of up to 200,000 people (COMEAP, 2010).

A number of studies have sought to identify whether a specific component of PM is mainly responsible for adverse health outcomes. Schlesinger (2007) reviewed studies of the health impacts of the inorganic components of PM and noted that the ability to distinguish effects within a complex mix is difficult and that no one single component is likely to be responsible for all adverse health outcomes. For example, Reiss et al (2007) note that virtually no epidemiological data exist in relation to the effects of nitrate on health outcomes. More recently there have been a number of studies that have reviewed the available literature regarding the health effects of the main components of PM (see for example Rohr and Wyzga, 2012, and Kelly and Fussell, 2012). Rohr and Wyzga (2012) found that there were no components for which there was unequivocal evidence of zero health impact although Kelly and Fussell (2012) concluded that there was generally less compelling evidence to connect secondary inorganic particles with adverse health effects.

Grahame and Schlesinger (2007) in their review found that whilst in most recent studies sulphate was not associated with adverse health outcomes this was not the case for components from traffic related sources. Most studies they considered found an association between traffic emissions (particularly elemental carbon from diesel emissions which are in the $PM_{2.5}$ and less size range) and lung cancer and cardiopulmonary effects with populations living closer to major roads at greatest risk. The later studies of Rohr and Wyzga (2012) and Kelly and Fussell (2012) arrived at similar conclusions. Ris (2007) observed that the ageing process of diesel emissions (gaseous and particulate) affects its toxicity with some compounds becoming less toxic and some more toxic. The effects may be both acute (respiratory irritant and asthma) and chronic (pulmonary injury and lung cancer). Lucking et al. (2008) demonstrated that inhaling diesel exhaust increases thrombosis formation but also consider "that risk is greatest in those with pre-existing cardiovascular disease."

Valberg (2004) was of the opinion that whilst the known major constituents of PM may each have limited toxic potential there may be synergistic interactions as well as antagonism or additivity between the components which need to be taken into account when considering the health impacts of 'simultaneous exposure to multiple chemicals'. Grahame and Schlesinger (2007) considered that a reduction in the "relatively benign" PM mass might actually accentuate the harmfulness of toxic emissions.

Heal et al. (2012) also noted that results emerging from health studies revealed a "negative impact" from traffic-related emissions and that metrics based on black or elemental carbon are better markers of this source. In its 2012 Review the WHO Regional Office for Europe stated that whilst black carbon may not be a major direct toxic component it may operate as a universal carrier of a wide variety of chemicals of varying toxicity (Janssen et al., 2012). A further report by WHO/Europe (2013) reviews the evidence on health aspects of air pollution and confirmed that there was no evidence of a safe level of exposure and that there was new evidence linking black carbon to cardiovascular health effects and premature mortality from both short and long term exposure. The report goes on to suggest that black carbon is a "valuable additional air quality metric for evaluating health risks of primary combustion particles" (WHO, 2013).

It is clear from the above that, to date, no unequivocal conclusions have been reached but there are now well documented adverse health effects associated with increased $PM_{10}$ and $PM_{2.5}$ including increased asthma attacks, attacks of chronic obstructive pulmonary disease (COPD), cardiovascular problems and deaths from heart attacks, strokes and respiratory causes. Maynard and Myers (2006) highlight that the exact mechanisms by which ambient particles damage health remains unknown and that some of the research has produced 'remarkable and unexpected findings', for example the strong link between cardiovascular disease and air pollution. Vehicle specific emissions, and in particular diesel particulate matter, are highly implicated in adverse health outcomes.

In order therefore to promote overall reductions in particulate matter arising from human activities and hence improve health outcomes in the general population it is important to have an effective regulatory regime in force based on current research and understanding of the processes involved.

# Regulatory framework in Europe and the UK

A regulatory framework in Europe and the UK seeking to control ambient PM arising from human activity continues to evolve and remains a dynamic process which has yet to provide a comprehensive safety net for human health or the environment. Details of the evolution of this regulation may be found in Williams (2004), AQEG (2005), Wilde (2010) and Heal et al. (2012). Williams (2004) makes the crucial point that the public desire to continue using coal in the mid-20th century was 'considerably weaker' than the desire of today's public to use their motor vehicles. Within Europe the mobile sources of PM referred to above are dealt with by seeking (a) to manage/restrict emissions (e.g. from transport) and (b) to regulate the upper limits of specified pollutants within ambient air.

## European vehicle emission standards

Since 1992 increasingly stringent standards, known as Euro standards, have been introduced under EU legislation requiring the reduction of emissions, including particulates, from new vehicles. Details of the standards are available via www.dieselnet.com. In summary, light goods vehicles less than 3.5 tonnes, together with passenger vehicles, have been subject to different regulations to heavy goods vehicles including buses. The standards for each category are usually differentiated by the use of Arabic numbers (Euro 1, 2, 3 etc.) for light goods vehicles and roman numerals for heavy goods vehicles (Euro I, II, etc.). Diesel and petrol engines have also, until recently, been treated differently. The current Euro 5 standard applied to the approval of new vehicles from September 2009 and all new sales from January 2011. Until the adoption of this standard particulate emissions from petrol engines were not regulated. The main effect of Euro 5 was to seek reduction of particulate emissions from diesel engines from 25 milligrams per kilometre (mg $km^{-1}$) to 5 mg $km^{-1}$ and introduce the same requirement for petrol engines. A particle number limit was also established for the first

time. Euro 6 is due to be introduced in 2014 but will not change the requirement in respect of particulate emissions. The standards for heavy goods vehicles, which included urban buses from 1999, are defined by energy output (g $kWh^{-1}$) rather than distance (making it difficult to compare the standards directly). Euro I, introduced in 1992, required a maximum output of 0.612 g $kWh^{-1}$ in relation to particulates. The current standard, Euro V1, introduced in 2013 requires 0.01 g $kWh^{-1}$. As a result of these requirements all new diesel engine vehicles need to be fitted with a diesel particulate filter (DPF). The Department for Transport propose to introduce a requirement for an inspection of the DPF to be part of the annual MOT test from February 2014 (www.gov.uk/government/news 4 December 2013).

Cames and Helmers (2013) consider that the preferential treatment of diesel engines over petrol engines in the EURO standards coupled with lower vehicle excise duty bands in the UK for diesel vehicles (introduced as a climate change measure in an attempt to lower $CO_2$ emissions) has led to an increase in the number of diesel vehicles in the UK fleet (often referred to as "dieselisation"). The European Petroleum Industry Association (EUROPIA) in its 2012 annual report note that diesel demand in Europe is expected to change from a 2:1 ratio in favour of petrol in the 1990's to a 1:3 projected demand in favour of diesel fuel by 2030. In the UK the Department for Transport Vehicle Licensing Statistics for 2012 indicated that the number of newly registered vehicles powered by diesel was more than 50% of new cars for the first time. It goes on to state that the proportion of the licensed cars fuelled by diesel had risen from 7.4% in 1994 to nearly 32.7%. The total number of licensed vehicles has also increased every year since 1991. The statistics also reveal that London has the lowest rate of vehicles per person in the UK (314/1000). TfL (2013) report a 10.9% reduction in road vehicle traffic in London between 2000 and 2012 but make no distinction between diesel and petrol driven vehicles.

There are currently no regulatory limits for emissions of PM which may arise from physical processes such as road abrasion or brake and tyre wear.

# Sulphur in Fuel

On 4 December 2007 it became mandatory for all retailers in the UK to sell ultra- low sulphur fuel (no more than 10 ppm) for use in vehicles as a result of the Sulphur Content of Liquid Fuels Directive 1999/32/EC. The Directive was extended in 2005 to cover marine fuels. The Baltic Sea, North Sea and English Channel were declared sulphur emission control areas (SECAs) and the fuel standard in respect of sulphur content was limited to 1.5%. A further amending Directive in 2012 (2012/33/EU) requires that the sulphur content of marine fuels should be reduced to 0.1% in SECAs and, in principle, a reduction to 0.5% elsewhere by 1 January 2020.

# EU Air Quality Framework Directive

In May 2008 a Directive on Ambient Air Quality and Cleaner Air for Europe (2008/50/EC) was adopted. It merged four directives, including the 1996 Framework Directive (1996/62/EC) and the first Daughter Directive (1999/30/EC) which dealt with particulates, into a single directive. Details of the 2008 Directive may be found at www.ec.europa.en/environment/air. In summary the standards in the 1999 Daughter Directive in relation to $PM_{10}$ were incorporated with no change to existing objectives. In respect of $PM_{10}$ this requires that a 24 hour mean of 50 $\mu g\ m^{-3}$ must not be exceeded more than 35 times a year - referred to as a Daily Limit Value (DLV) - together with an annual mean of 40 $\mu g\ m^{-3}$. For the first time $PM_{2.5}$ has been regulated with an exposure reduction target.

'Limit value' is defined as "a level fixed on the basis of scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained within a given period and not to be exceeded once attained."

If levels are already lower than the limit values then PM levels must be maintained below the limit values and Member States must "endeavour to preserve the best ambient air quality, compatible with sustainable development."

It may also be possible, under certain circumstances, to discount natural sources of pollution which are "not caused directly or indirectly by human activities", for example sea-salt, when assessing compliance against limit values (EC, SEC 208, 2011). The UK has used this provision seeking to achieve compliance in respect of the Greater London area (Defra, 2009). Brookes et al. (2012) set out the method, which is based on chloride measurements, for estimating the number of days with a PM10 concentration greater than 50 μg $m^{-3}$ associated with a contribution from sea-salt.

Finally the Directive requires member states to introduce air quality strategies and sets out monitoring and assessment obligations.

The EU instigated a review of EU Air Policy in 2011 and designated 2013 as the "Year of Air". A new Clean Air Programme for Europe was announced in December 2013 seeking to ensure that existing targets are met in the short term and proposing new targets up to 2030 (EC Press Release, 18 December 2013, IP/13/1274)

## Air Quality Strategies and their implementation

In the UK air quality strategies and action plans are required to be drawn up by all tiers of government, national and local.

The Air Quality Strategy for England, Scotland, Wales and Northern Ireland was published in July 2007. New measures under consideration in the Strategy included promoting the uptake of low emission vehicles, reducing emissions from ships, national road pricing and retrofitting catalyst-based particulate filters to Heavy Goods Vehicles (HGVs).

In London, the Mayor of London has responsibility for air quality and transport in London. The Mayor's Air Quality Strategy entitled "Clearing the Air" was published on 14 December 2010 by the Greater London Authority (GLA, 2010). The Strategy reported that there were more than 4000 premature deaths per year in London due to poor air quality and that people living in deprived areas are disproportionately affected by poor air quality. The Strategy includes introducing age limits for taxis, promoting low emission vehicles and retrofitting older buses.

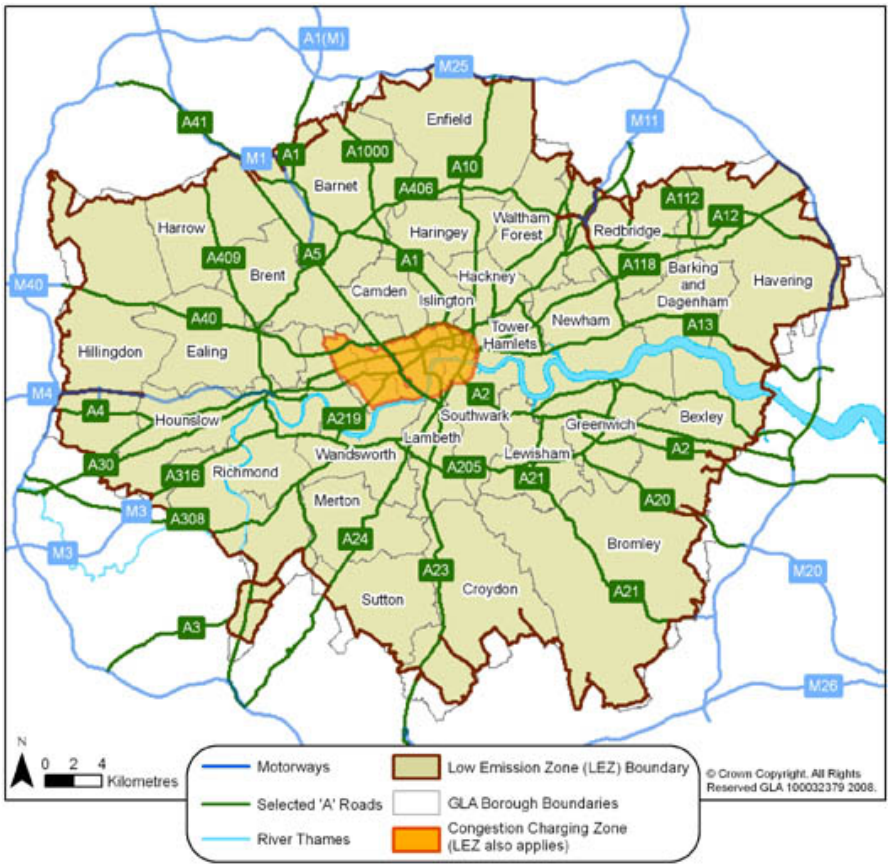
The Greater London Authority was established in 2000 (its predecessor the Greater London Council having been abolished in 1986). The Authority has implemented a number of strategies seeking to improve air quality in London. Transport related schemes are managed by Transport for London ("TfL") as part of the GLA. The flagship initiative has been the phased implementation of a Low Emission Zone (LEZ) beginning in 2008. It is based on the Euro standards described above. HGVs more than 12t gross vehicle weight (GVW) were required to meet Euro III standards in February 2008 followed by vehicles between 3.45t and 12t in July 2008. Failure to comply resulted in a daily fine. These requirements were tightened in January 2012 and these vehicles were required to meet Euro IV standards and vehicles between 1.2 and 3.5t were required to meet Euro 3 standards for the first time. The daily penalty was increased at the same time. Figure 1.6 is a map showing the area of the Low Emission Zone and as may be seen it covers almost the whole of the Greater London area. Kelly et al. (2011) carried out a study in 2007 prior to the introduction of the London Emission Zone in order to provide a baseline against which change could be assessed. Jones et al. (2012) noted a reduction in particle number concentration at a number of sites in London at the beginning of 2008 but as the introduction of low-sulphur fuel occurred at the same time as the introduction of the Low Emission Zone it was difficult to be certain as to which scheme might be responsible (or indeed either) but concluded that the introduction of low-sulphur fuel was more influential on the reduction of particle numbers. Ellison et al. (2013) concluded that the introduction of the LEZ had a substantial effect on the composition of the vehicle fleet in London and that London's air quality had improved "marginally" with reductions in concentrations of PM10. Boogard et al. (2012) considered the impact of a similar scheme introduced in the Netherlands and found that the policies were 'too modest' to produce improvements in traffic-related air quality.

Also indicated on the map in Figure 1.6 is a small central area referred to as the congestion charging zone which is also managed by Transport for London (TfL). Congestion charges (Monday to Friday, 7a.m. to 6 p.m.) were introduced in February 2003. The original intention was to alleviate congestion from traffic in central London by imposing a daily charge for driving in the zone. Some discounts were offered under a scheme called the Greener Vehicle Discount. This scheme ended in July 2013 because it preferentially benefited vehicles with small diesel engines although a 'sunset period' of three years remains for vehicles already

registered under the scheme. At the same time an Ultra-Low Emission discount was introduced whereby electric vehicles together with cars and vans that meet Euro 5 standard may qualify for a 100% discount. TfL considered that one of the benefits of this scheme would be to reduce air pollutants (www.tfl.gov.uk).

Atkinson et al. (2009) considered the impact of the congestion charging scheme on air quality in London but found that it was difficult to dissociate its introduction from other traffic management schemes introduced at the same time but they reported 'unexpected' results of an increase in background $NO_2$ and $O_3$.

*Figure 1.6 Map of London's Low Emission Zone and Congestion Charging Zone*




Courtesy of Greater London Authority

## Local air quality management

To date, the role of the local authority has been pivotal in providing local air quality management. Each local authority is required to carry out a review and assessment of air quality in its area and, if national air quality objectives in respect of any pollutant are unlikely to be achieved, declare an Air Quality Management Area (AQMA). All the London Boroughs have declared an AQMA (www.aqma.defra.gov.uk). Defra instigated a review of this process in July 2013 and have indicated a desire to abolish AQMA's in order "to release officer time to take action on air quality." A number of institutions have voiced their concerns (ENDS Report 465, November 2013). No decision has yet been made.

For a local authority to implement any strategy which involves seeking to improve air quality it needs to set up a monitoring method which provides typical information suitable as a baseline for the situation which is likely to produce the main problems in meeting the standards. The local authority also has to work within the constraints of a limited budget and other resources such as manpower.

# Measurement methods

It is difficult to predict or control ambient levels of PM based on knowledge of emissions alone. The composition of ambient air needs to be sampled and measured directly to assess the success or otherwise of control strategies. Details of current air quality monitoring networks in the UK are set out in Table 3-2 of Defra's report 'Air Pollution in the UK 2012' (Defra, 2013). The networks fall within two broad categories: those which are required to fulfil the statutory obligations imposed by the 2008 Directive (2008/50/EC) and those which are for research purposes only.

# Measurement of Ambient $PM_{10}$ and $PM_{2.5}$ to meet statutory requirements

Concentrations of $PM_{10}$ and $PM_{2.5}$, as previously stated, are subject to regulatory limits and therefore need to be monitored for compliance purposes. Within the UK, measurements of $PM_{10}$ and $PM_{2.5}$ are carried out as part of the Automatic Urban and Rural Network (AURN) which had 131 sites in 2012 (Defra, 2012). In addition these species are also monitored within the London Air Quality Network (LAQN) which formed in 1993 and is operated and managed by the Environmental Research Group (ERG) at King's College, London (KCL). Most local authorities have at least one site which monitors/measures $PM_{10}$ in their area and the location of a sampler will vary depending on the baseline information required but typically is at a kerbside, roadside (up to 5m from the kerb), urban background, suburban or rural location. The majority of the London boroughs supply details of their sampling programme to ERG and details are available to download (www.londonair.org.uk). A series of annual reports are published and are available for download from the website – see for example Mittal et al., 2013.

The 2008 Directive (2008/50/EC) currently requires that PM should be measured gravimetrically in accordance with EN12341 (in relation to $PM_{10}$) issued by the European Committee for Standardisation (CEN, 1999) and EN 14907 (in relation to $PM_{2.5}$) (CEN, 2005). In February 2011 CEN published a working document (CEN/TC/264) giving details of a proposal to merge both standards but this is yet to be implemented.

In the UK the two principal measurement methods in current use are Tapered Element Oscillating Microbalances (TEOMs) and filter based gravimetric samplers (most commonly the Partisol 2025 supplied by Rupprecht and Patashnik).

# TEOM based measurements

TEOMs are continuous analysers which consist of a filter cartridge located on top of a hollow tapered glass element. The element is clamped at one end and free to vibrate at the other. The sample air stream is drawn through a filter and then through the element. Constant flow through the system is maintained by a mass flow controller unit. The glass element vibrates at its natural frequency and as particles are deposited on the filter the frequency of vibration decreases. An accurate measurement of the change in frequency yields a measure of the accumulated mass which is then divided by the flow rate to provide a particle mass concentration (DETR, 2000).

In the UK TEOMs have been widely installed by local authorities because they were the original UK reference method and they have the advantage that they record mass concentrations measurements in "real-time" allowing high concentration episodes and diurnal variations to be readily identified. However, in a TEOM the sampling stream and filter are heated to 50°C to maintain a stable temperature and eliminate interaction between water and particulate matter on the filter. There is consequently a loss of volatile species, particularly ammonium nitrate (see e.g. Allen et al.,1997, Ayers et al., 1999, Price et al., 2003, Charron et al., 2004). Charron et al. (2004) point out that the TEOM instrument may, as a consequence of this loss, miss events above the DLV.

Local authorities were originally advised to apply a 'correction factor' of TEOM x 1.3 to achieve data which would be equivalent to a gravimetric measurement. This is in addition to a pre-installed correction factor within the sampler (=1.03 * TEOM mass +3) complying with US EPA requirements – see Green and Fuller (2006) for more details. Green et al. (2001) compared data from gravimetric and TEOM measurements and concluded that this correction factor also needed to include local geographical and temporal (i.e. summer versus winter) variability. Measurements are reported at Standard Temperature and Pressure (STP) but Green and Fuller (2006) found that this inflated PM mass concentration levels and recommend that the measurements be reported at ambient temperature and pressure.

Harrison (2006) reported on a range of studies testing the equivalence of a number of samplers in order to meet the EC Guidance on Equivalence published in November 2005 (EC, 2005) and concluded that the TEOM by itself did not meet the equivalence criteria even with the correction factor applied but TEOMs retrofitted with a FDMS (Filter Dynamic Measurement System) did so. The FDMS system is based on TEOM technology and automatically measures mass concentrations including non-volatile and volatile PM components (Green et al., 2006). Local authorities are being encouraged to use instruments that conform to equivalence criteria, particularly when purchasing new instruments or replacing old ones. However, in the meantime DEFRA, recognising that many local authorities have invested "considerable resources" in TEOM analysers, has identified a model known as the Volatile Correction Model (Green et al., 2009) which may be used throughout much of the UK including London to correct TEOM data to a concentration that is equivalent to the reference method. The model removes the USEPA correction, corrects for the losses of volatile species based on measurements from nearby FDMS instruments and reports the measurements at ambient temperature and pressure. DEFRA recommends in its Technical Guidance (2009) that TEOM data should be adjusted using this model wherever possible.

## Gravimetric samplers

Gravimetric samplers collect particles by using pumps to draw air through a filter paper. A common gravimetric sampler in use in the UK is the Partisol 2025 sequential air sampler which allows for up to 16 days continuous monitoring with an automatic filter exchange (www.thermoscientific.com). Air is drawn through a size-selective inlet ($PM_{10}$ or $PM_{2.5}$) at a rate of 1 $m^{-3}$ $hr^{-1}$ and particles are collected on a 47 mm filter. Filter exchange usually takes place every 24 hours but other time periods could be selected. Choice of filter substrate may be influential and is discussed in more detail in chapters 2 and 3. There are also potential sampling artefacts associated with gravimetric samples. Price et al. (2003) considered that some of the discrepancies between TEOM and gravimetric concentrations are as a result of

particle bound water on the filter increasing the amounts of particulate matter recorded by the gravimetric monitor. This aspect has been further explored by Maggs et al. (2008) and is discussed in more detail in chapter 3. Weighing and conditioning of filters both before and after sampling might also introduce artefacts. Whilst real-time measurements are not available a filter-based sampling method provides samples which may be subjected to other subsequent analysis (for example ion chromatography or metal analysis).

# Non statutory measurements made for research purposes

There are a number of different air quality networks monitoring a variety of different pollutants set out in Table 3-2 of Defra's Air Pollution in the UK 2012 report. Of particular interest to this research project are two networks, namely the Particle Concentrations and Numbers Network and the Black Carbon Network.

## Particle concentrations and numbers

Details of the airborne particulate concentrations and numbers network in the United Kingdom are set out in a series of annual reports – see for example Beccaceci et al., 2013. There are 5 sites in the network, two of which are in London: North Kensington and Marylebone Road. Filters are collected using a Partisol 2025 sampler and subsequently analysed for sulphate, nitrate and chloride by ion chromatography and EC/OC using the NIOSH-TOT method (which is discussed in more detail in chapter 2). Details of this analysis are publicly available.

# Black Carbon Network

The Black Carbon Network in the UK has evolved out of the UK Smoke and Sulphur Dioxide Network which had a long history in the UK and was originally set up in London in the 1920s as the British smoke shade (BSS) method (Brimblecombe, 1987).

At one stage there were more than 1200 sites in the UK set up as part of the UK Smoke and Sulphur Dioxide Network (Fowler et al., 2005). Approximately 2 $m^3$ ambient air was sampled daily by being drawn through a cellulose filter at a constant flow rate of 1.4 l $min^{-1}$ using an 8 port Black Smoke sampler. Particles of an approximate size fraction of $PM_{4.5}$ were collected on the filter and the blackness of the resulting stain measured by the local authority using an EEL (Evans Electroselenium Ltd) smoke stain reflectometer. A broadband light is shone on the loaded side of the filter sample and the amount of reflected light is measured. Loss of reflectance was attributed to the light absorbing properties of the staining particles. This measurement was converted to a PM mass measurement using the British Standard Smoke Calibration Curve (BS 1747 Part 2, 1969) originally determined in the early 1960's and based on domestic coal smoke. In 1964 the Organisation for Economic Co-operation and Development (OECD) set up an equivalent standard (Publication number 17913). The Smoke and Sulphur Directive 80/779/EEC gave the OECD calibration as the reference method and to achieve equivalence the British Black Smoke ($BS_{(British)}$) measurements were corrected by multiplying by 0.85.

In 1993 the ISO (International Organization for Standardization) published ISO 9835: "Ambient air – Determination of a black smoke index". The blackness of the stain on a filter sampled by the method described above was measured in the same way but, instead of converting to a mass concentration using BS1747 or the OECD calibration, an absorption coefficient based on Lambert's Law (also known as the Beer-Lambert's Law), a mathematical expression of the relationship between absorbance of light and the concentration of an absorbing species, was derived. This absorption coefficient could then be further converted

to "traditional black smoke units" using a calibration curve in terms of the area of the stain on sampled Whatman No 1 filters and the volume of air sampled as set out in Annex A to the document.

The original calibration was determined when the use of coal was ubiquitous. Ball and Hume (1977) carried out a study in London in 1975 and 1976 noting a significant correlation between dark smoke (reported as $BS_{(British)}$) and airborne lead (Pb). Prior to 2000, Pb was added to vehicle fuel and was therefore, at that time a good indicator of vehicular emissions. Ball and Hume (1977) concluded that vehicles were "the dominant source of dark smoke in the entire Greater London area". They noted that this represented a fundamental change from the situation immediately after the introduction of the 1956 Clean Air Act. Bailey and Clayton (1982) also noted that patterns of energy use and transport were changing in the UK and concluded that a single calibration curve had become inadequate to describe the relationship between black smoke and gravimetric measurements but the Standard Smoke method was a "reasonably accurate measure of the concentration of carbon in the suspended particles".

In 2003, as part of its review of the health aspects of, *inter alia*, particulate matter, the World Health Organisation (WHO, 2013) concluded that the conversion of a reflectance measurement to PM mass had been demonstrated by Hoek et al. (1997) to be no longer valid because the ratio varied substantially with time, location and season but recommended that the 'value of black smoke as an indicator for traffic-related air pollution' should be 're-evaluated' because black smoke could serve as a useful marker in epidemiological studies, possibly with retrospective analyses using historic data. In 2005 the WHO published 'Health effects of transport-related air pollution' (WHO, 2005) in which it recommended the continued use of black smoke measurements because it was a more sensitive marker of traffic-related PM and in particular diesel vehicles. The report also noted that its advantages include ease of analysis and low cost.

In 2005 an independent review of the UK Smoke and Sulphur Dioxide Network was carried out by Fowler et al. (2006) on behalf of DEFRA and they recommended that sulphur dioxide need not be centrally monitored any longer but up to 20 sites should be retained nationally to monitor black smoke because they remained valuable particularly for health assessment. In 2006 the National Physical Laboratory (NPL) set up the UK Black Smoke Network on behalf of DEFRA (Butterfield et al., 2007). Of 21 sites throughout the UK selected to monitor black smoke using the method outlined above, 3 were in London: Sites at Woolwich (urban background) and Marylebone Road (kerbside) were retained and a new site set up at North Kensington (urban background). A Black Smoke Index (BSI) with units of $\mu g\ m^{-3}$ continued to be derived by using the relationship set out in BS 1747, Part 2, 1969.

In 2008 the Smoke and Sulphur Dioxide network was replaced by the UK Black Carbon Network ('BC Network') and black smoke samplers were replaced by model AE22 Aethalometers (Magee Scientific). A description of this measurement method is set out in annual reports dealing with the revised network – see for example Butterfield et al., 2011. In summary aethalometers quantify black carbon collected on a quartz tape by the change in absorption coefficient measured by a single pass transmission of light through the sample measured relative to a clean, blank filter. The aethalometers in the BC Network operate at two wavelengths, 880 nm and 370 nm. The infrared wavelength (880 nm) is used to measure the black carbon component. There are two sites within London, Marylebone Road and North Kensington, which are part of this Network.

Quincey (2007) compared automated Black Smoke measurements made at Marylebone Road in October/November 2006 with contemporaneous Black Carbon measurements from a Magee AE22 aethalometer (using quartz fibre filter tape) and found that the results 'should be inter-convertible'.

# Sources of variation in ambient levels of $PM_{10}$

AQEG (2005) discusses the relationship between $PM_{2.5}$ and $PM_{10}$ and observed a significant trend for the proportion of $PM_{2.5}$:$PM_{10}$ to increase with increasing $PM_{2.5}$ but less so with increasing $PM_{10}$ indicating a trend for variations in daily $PM_{10}$ to be driven by variations in $PM_{2.5}$ with a more constant contribution from the coarse fraction. A study of research projects carried out contemporaneously at 31 sites across Europe (including 3 sites in the UK) by Van Dingenen et al. (2004) and Putaud et al. (2004) noted that $PM_{10}$ and $PM_{2.5}$ annual average concentrations vary by more than a factor of 10 between the lowest and highest sites and that the ratio between the two size fractions also varies from site to site although individual sites have a characteristic relationship. Furthermore, the ratio increases with $PM_{10}$ levels indicating, it is concluded, that 'pollution periods' are predominantly due to increases in the mass concentration of $PM_{2.5}$. Heal et al. (2005b) also found variability in daily $PM_{10}$ in Edinburgh was more closely associated with variation in $PM_{2.5}$ than variation in PMcoarse and that days of high $PM_{2.5}$ were not also strongly associated with high PMcoarse levels reporting little correlation between $PM_{2.5}$ and PMcoarse ($r^2 = 0.10$).

Derwent et al (2009) considered that $PM_{2.5}$ mass concentrations in rural southern UK would be influenced by reductions in $SO_2$, $NO_x$ and $NH_3$ emissions "in a complex and interlinked manner" such that policy makers should consider focusing on the abatement of $NH_3$ (ammonia) to secure the largest $PM_{2.5}$ reduction. As previously noted, the majority of ammonia is produced by agricultural practices particularly animal manures from intensive production systems with housed animals and the application of mineral nitrogen fertilisers (Oenema et al., 2012). Velthof et al. (2010) noted that the majority of ammonia emissions in Europe were derived from housing and manure storage systems and apportioned emissions in Europe between manure and fertiliser application as 29% and 19% respectively with the highest ammonia emission hotspots being Belgium, the Netherlands, North West Germany, Brittany, France and the Po Valley in Italy. Furthermore Velthof et al. (2010)

pointed out that the Nitrate Directive (91/676/EEC) introduced closed periods in the autumn and winter for manure application leading to more applications during the Spring when the uptake efficiency was improved by being applied during the growing season but may lead to greater ammonia emissions as a result of warmer, drier conditions.

Harrison et al. (2004) compared days when the PM10 was greater than 50 μg $m^{-3}$ (i.e. days when the DLV was exceeded) with all days within their study at sites in London and Birmingham and noted a five-fold increase in fine particle nitrate and a twofold increase in all other components except sodium chloride in the roadside increment. Similarly Putaud et al. (2004) noted that nitrate concentrations may be greater than organic matter concentrations in both PM10 and PM2.5 on days when PM10 exceeds 50 μg $m^{-3}$ and that these episodes are often observed in cold periods. Charron et al. (2007) found that the regional background aerosol, and especially particulate nitrate, was the largest contributor (60%) to elevated episodes of PM10 concentrations at Marylebone Road during 2002 to 2004 with local traffic emissions the second largest contributor. They also noted that there was seasonal variability with more elevated episodes in March to April and October to December.

Yin and Harrison (2008) applied their pragmatic mass closure model to data collected at three sites in Birmingham and found that nitrate (adjusted for particle-bound water in accordance with their model) accounted for almost 50% of PM2.5 and 40% of PM10 on high episode days emphasising the need to understand the sources of nitrate and their control to achieve abatement. Abdalmogith and Harrison (2005) observed the role of nitrate in PM10 during high episode events in the UK and considered that the control of NOx emissions in the UK and adjacent Western European countries may have a major role in achieving a reduction in daily concentrations. A number of other studies (see, for example, Kleeman et al.,2005, Baker and Scheff, 2007) have also concluded that regulatory strategies need to focus on reductions in NOx emissions. In a study in Beijing Kai et al. (2007) also found that concentrations of nitrate increased most during pollution periods and the transformation rate of NOx to nitrate was five times higher during polluted periods. Ying et al. (2009) concluded in a study in California that diesel engines produced twice as much particulate nitrate as catalyst equipped gasoline engines and that between them they accounted for up to 60% of secondary nitrate. Kleeman et al. (2005) point out that the dynamics of the formation of ammonium nitrate is non-linear and therefore a reduction in precursor species

does not achieve a commensurate reduction in ammonium nitrate. They predict that a 50% reduction in local NOx leads to 25% less nitrate. In their study in California, US they estimated that almost half of the nitrate aerosol was from local sources and the remainder was from areas upwind of the study site highlighting the need for the control of all emissions and sources.

Charron et al. (2007) concluded that emissions which would have arisen solely in the UK were less frequent contributors to high episodes although Fuller and Green (2004) and Charron and Harrison (2005) found that local building and road works (in the vicinity of, inter alia, Marylebone Road) could contribute to breaches of the EU daily limit value.

In summary, differences between the mass concentrations and chemical components of PM have been found in the two main size fractions and their contribution would appear to vary from site to site as well as day to day. It is also not necessarily a typical composition at various sampling sites which is the only consideration when assessing health outcomes and trying to define control/ abatement strategies. It would seem that it is also important for local and other regulatory authorities to understand the causes of "pollution periods" particularly at varying locations, what is happening in the different size fractions and their components and how these differ from other days in order to ameliorate or control emissions such that these events may be managed and their impact reduced as far as possible.

Strategies to improve air quality by reducing airborne particulate matter ($PM_{10}$) and its components are at the forefront of government thinking, internationally, nationally and at a local level. There is a need to understand whether the suite of regulatory and other initiatives, such as the LEZ and changes in monitoring and measurement methods, introduced in London during the last ten years have been influential in bringing about change in London's air quality in order to inform future strategies.

# Research Aims

To examine PM mass and its component inorganic and carbonaceous species at a number of locations in London during the period 2001 to 2012 by

- applying existing methods to measure PM composition, and
- developing new simple approaches for the quantification of equivalent black carbon;

in order to:

a) understand changes in concentrations over time, particularly high pollution days;

b) improve understanding of the impact of air quality initiatives introduced to date.

# Objectives

- To compile datasets, using PM measurements collected at different locations in London, based on consistent methodology, and its component analysis between 2001 and 2012, from
  (i) field and laboratory measurements carried out as part of this research project;
  (ii) publicly available data; and
  (iii) other available research.

- To develop a method for determining atmospheric particulate carbon in PM using archived filters both retrospectively and at sites where only PM (gravimetric) measurements are made.

- Systematically evaluate these datasets to consider and compare differences and similarities in concentrations of the different species at and between the different locations.

# Chapter overview

Details of the main study sites, compilation of the datasets, including methodologies used, and analytical methods are set out in **chapter 2**.

In each of the following chapters results and discussion of findings are reported together.

Mass concentrations of PM10 and PM2.5 are currently the only regulatory metric in use and therefore the only metric against which improvement may currently be measured. In **chapter 3** the mass concentrations of all the PM collected at the study sites are grouped according to concentration and compared both to each other and over time to evaluate whether change has occurred in this metric.

Due to the generic nature of PM10 it is the components which are of most importance in determining change. Concentrations of the inorganic components of PM (again grouped according to its concentration) at the study sites are compared in **chapter 4**.

Traffic emissions are increasingly implicated in poor health outcomes but determining PM10 from those emissions over time is more difficult due, in part, to changes in monitoring regimes. In **chapter 5** methodologies for ascertaining equivalent black carbon concentrations, a key indicator of diesel traffic emissions, from retrospective carbon analysis using a transmissometer are developed. Additionally, a measurement of black carbon is embedded in historic black smoke data where reflectometry was used to measure light-absorbing particles. A comparison between reflectometry and transmissometry measurements carried out on the same filter and its contribution to current research seeking to convert black smoke measurements to black carbon are further discussed. Important implications of using different filter substrates are identified.

In **chapter 6**, Equivalent black carbon concentrations in PM10 based on the methodologies developed in chapter 5 are calculated for each study site, including Oxford Street, and compared over time. The opportunity is taken to extend calculations of black carbon concentrations to the historic black smoke data to compare change over an extended time period.

**Chapter 7** draws together the findings of this study in the context of the research aims and objectives set out in chapter 1 followed by a discussion of the key findings. Some possible directions on future research work are included.

# Chapter 2

# Data collection and analysis methods

## Introduction

To achieve the research aims set out in chapter 1, it was necessary to have measurements of concentrations of PM10 and its components at different types of sites in London for the period 2001 to 2012. The measurements used in this thesis have been drawn from a number of sources, as follows:

- A field sampling campaign carried out at Acton Town Hall in west London as part of this project and reported here in detail for the first time.
- Publicly available datasets from the London Air Quality Network and Defra regarding sampling carried out at Marylebone Road, North Kensington and Oxford Street, all in central London and black smoke measurements carried out at Marylebone Road and Greenwich High Road.
- Other research carried out by the Environmental Research Group (ERG) at King's College, London (KCL) which has been made available for this project.
- Archived filters stored at KCL.

These datasets yielded, in the first instance, measurements of

- $PM_{10}$ and $PM_{2.5}$ mass concentrations,
- concentrations of secondary and natural sources represented by selected anions (sulphate, nitrate and chloride),
- elemental carbon concentrations.

Concentrations of $PM_{10}$ and its main components have been assessed and compared over time. In this chapter, descriptions of the study sites together with details of the data collection and analysis methods are described.

# Study Sites

As the Environment Agency point out in their Technical Guidance Note M8 (2011) "it is rare to find a perfect monitoring location" and there is often a compromise between competing considerations. In this study data from five well-established monitoring locations, all within the London Air Quality Monitoring and/or the black smoke network of sites have been used. The sites are:

1. **Acton Town Hall**
2. **Marylebone Road**
3. **Oxford Street**
4. **N Kensington**
5. **Greenwich High Road**

## 1. Acton Town Hall Grid reference 520180

This was a suburban roadside site situated at the crossroads of High Street Acton and Winchester Street in the grounds of Acton Town Hall in the London Borough of Ealing, west London. The sampler was situated relatively close to the town hall building but there was nevertheless a free flow of air around the sampler. During the study period, approximately 14,000 vehicles travelled on the east-west route (High Street) and 4,000 on the north south arm daily. In the morning peak hour (8 – 9am) 900 vehicles travelled through the junction towards London (west – east) whilst more than 500 passed in the opposite direction. The traffic was a mix of commercial, public transport (buses) and domestic vehicles. Vehicles did not usually pass through the junction at speed because of the traffic lights. Queues built up but tended to clear within one phase of the traffic lights. The study site was characteristic of many town centres both within Greater London and elsewhere. The suburban location was typical of places where people live, work, shop and carry out leisure pursuits (for example visiting the adjacent swimming pool or the nearby park). The sampling site closed in January 2012 and the area has since been redeveloped.

## 2. Marylebone Road, Grid reference 528182

A kerbside site in the City of Westminster, central London. The site is often referred to as the 'Supersite' as it is one of the main monitoring sites in London. The monitoring station is contained within a standalone cabin alongside the A501 which is a heavily trafficked six lane highway which acts as an east-west arterial route into and out of central London. The highway is often congested. Between 1999 and 2001 an average of more than 80,000 vehicles per day travelled along Marylebone Road (both directions). This figure dropped between 2002 and 2012 to between 73, 000 and 77,000 vehicles. The surrounding buildings, which are mainly a mixture of offices and shops, enclose the road and may cause what is often referred to as a 'canyon effect' (see below). There are also a large number of pedestrians in the area some of whom are tourists visiting nearby attractions such as Regent's Park and Madame Tussaud's waxworks.

## 3. Oxford Street, Grid reference 528181

A kerbside site on a busy world-renowned shopping street in the City of Westminster, in the West End of London running parallel and to the south of Marylebone Road. There are approximately 300 shops with a high number of pedestrians, comprising shoppers and tourists. More than 100,000 pedestrians per day pass the busiest points. Only buses and taxis are allowed to travel along the length of Oxford Street. Twenty-three (23) bus routes use all or part of the length of Oxford Street operated by seven different bus companies. There are approximately 160 buses per hour rising to more than 300 per hour during the peak hours. Traffic moves very slowly: bus operators schedule buses to take 22 minutes to travel the 1.5 miles. Taxis use up approximately 30% of the available road space (GLA, 2010).

## 4. N Kensington, Grid reference 524181

An urban background site situated in the grounds of the Sion Manning School, St Charles' Square in the Royal Borough of Kensington and Chelsea. The school is situated on a quiet residential road within a residential area. The area is not heavily trafficked.

## 5. Greenwich High Road Grid reference 538177.

A black smoke monitoring site operated by the London Borough of Greenwich that closed in 2008. The area is suburban in character and comprises a mix of residential, shops, offices and restaurants often frequented by tourists. More than 12,000 vehicles travel along it each day.

Site maps showing each location are illustrated in Figure 2.1 and photographs of each LAQN site are shown in Figure 2.2. No photograph is available of the site in Greenwich High Road. The photographs of Marylebone Road, Oxford Street and North Kensington are courtesy of the Londonair website (www.londonair.org.uk).

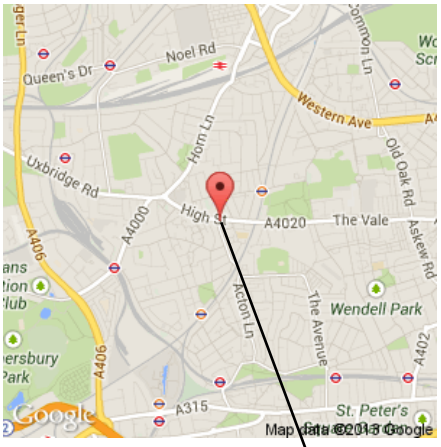
Whilst the composition of the traffic fleet at each site would undoubtedly have changed from day to day and over time, the physical characteristics of each site remained constant throughout the study period. Each of the sites had a predominantly west-east orientation and therefore meteorological influences such as wind direction and wind speed would have been similar at each site.

Vardoulakis et al (2003) point out that "street canyon" is frequently used to describe urban streets flanked by buildings on both sides and the term has often been applied to the layout at Marylebone Road (see for example Jones and Harrison (2005), Thorpe et al., 2007 and Vardoulakis et al., 2007). When considering the influence of wind direction on concentrations, Jones & Harrison (2005) pointed out that a "cross canyon wind will induce a vortex in the canyon resulting in the direction of the air flow at street level being reversed". Under certain meteorological conditions (mainly when the wind was from the south or west) PM concentrations were heavily dominated by emissions within the street canyon. Oxford Street has a similar layout and may also be considered to be a "street canyon". Marylebone Road and Oxford Street run in a west-east direction parallel to each other and are very close geographically (see Figure 2. 1). It may be expected that meteorological and other physical conditions at each site are very similar and therefore direct comparison between the two sites of concentrations of PM (and its sources in later chapters) may be inferred.

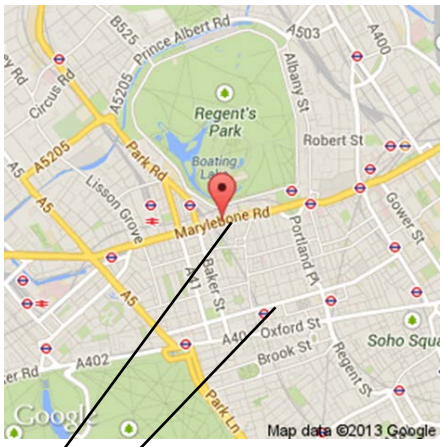
All of the sites are within the Low Emission Zone. Marylebone Road forms the northern boundary of the congestion charging zone but does not fall within it.

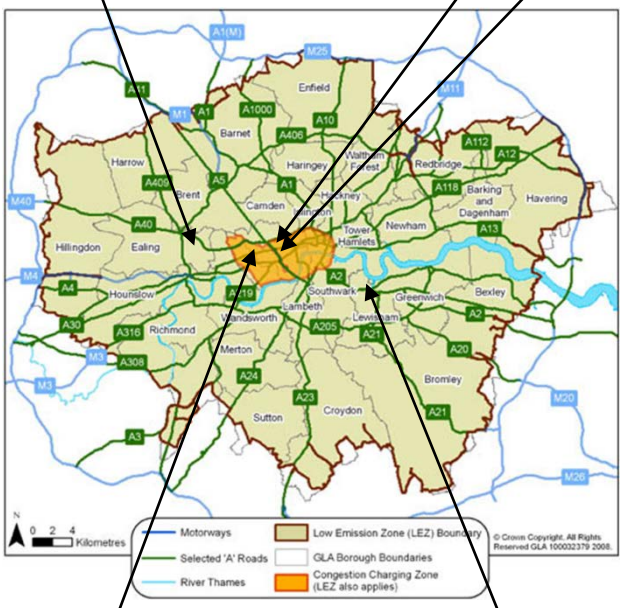
*Figure 2.1 Location of each study site (Acton Town Hall, Marylebone Road, Oxford Street, North Kensington and Greenwich High Road) within the Greater London area*

*Acton Town Hall*

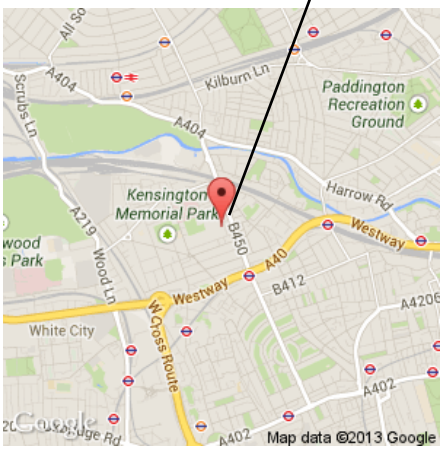



*Marylebone Road and Oxford Street*




*North Kensington*




*Greenwich High Road*


*Maps courtesy of Google maps*

*Figure 2.2 Site photographs*

*(a) Acton Town Hall*


*(a) taken from train crossing Acton High Street east of the site*

*(b) taken from Winchester Street west of the site*

*(b) Marylebone Road*

*Figure 2.2 Site photographs (continued)*

*(c) Oxford Street*

*(d) North Kensington*

# Data Collection

## PM10 and PM2.5 mass concentrations

All of the PM mass concentration data in this research project were collected on a daily basis using Partisol 2025 ('Partisol') , low volume, gravimetric samplers manufactured by Rupprecht and Patashnick, now part of Thermo Fisher Scientific, NY 12061, US.

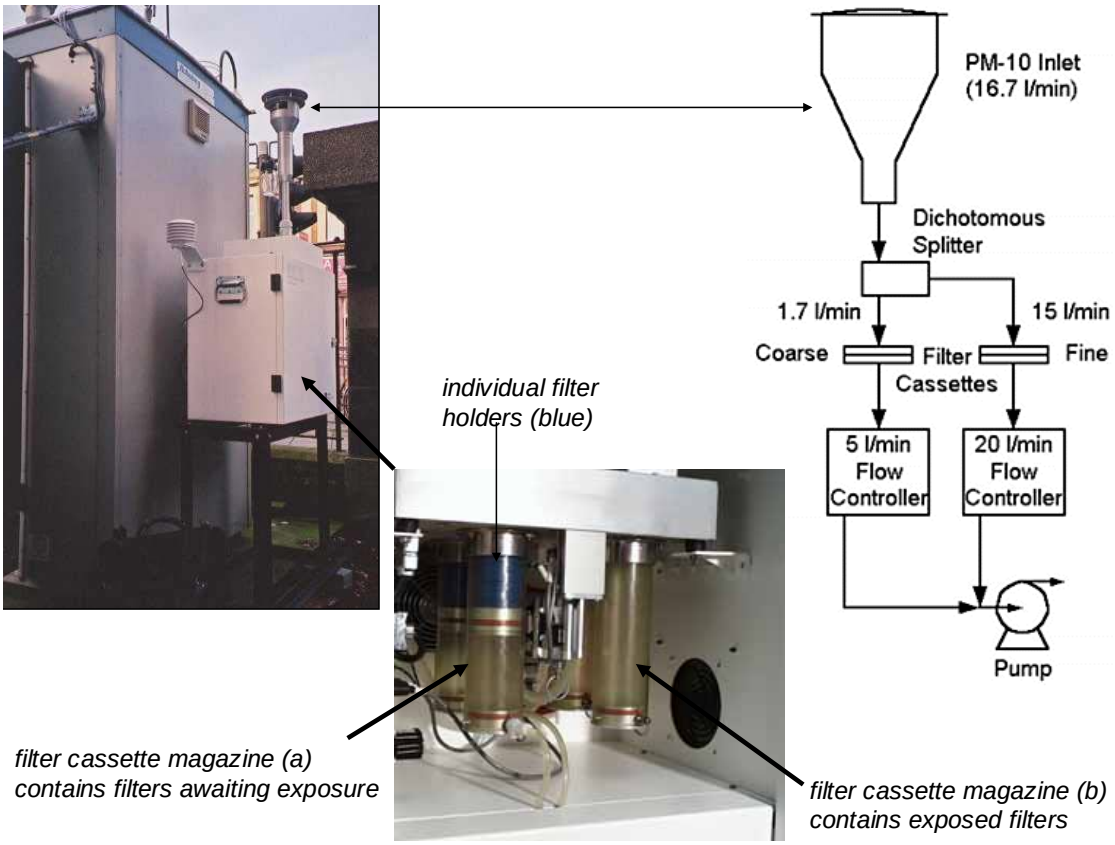
The most common filter substrates used with a Partisol are made from PTFE ('Teflon'), quartz fibres, cellulose and PTFE bound glass fibre ('Emfab$^{TM}$'). Choice of filter substrate depends on a number of factors, for example, collection performance during high or low episode periods and the nature of any desired subsequent chemical analysis. CEN Standards EN 12341 and EN 14907, issued by the European Committee for Standardisation in 1999 and 2005 respectively, currently specifies that quartz filters should be used for reporting gravimetric measurements although consideration is currently being given to changing the CEN standard to Emfab$^{TM.}$ (CEN, 2011). Emfab$^{TM}$ filters were not available at the time of the sampling campaign at Acton Town Hall (2001 – 2002).

### PM sampling at Acton Town Hall 2001 – 2002

A Partisol dichotomous sampler was deployed at Acton Town Hall during 2001 and 2002. It was fitted with a standard PM10 inlet, which samples air at approximately 2 m above ground level, operating at the inlet's design flow rate of 16.71 l min $^{-1}$ (1 m$^3$ h$^{-1}$), i.e. equivalent to the human lung ventilation rate. The initial particle size cut off has a diameter of 10 μm. Thereafter the particle stream is split by means of two separate constant flow rates (15.0 l min $^{-1}$ and 1.71 l min $^{-1}$) into two size fractions, a coarse fraction (PM 2.5 – 10) and a fine fraction (PM≤2.5) collected simultaneously on two separate 47 mm filters. (The descriptions PMcoarse / PM 2.5 – 10 / the coarse fraction and PM fine / PM2.5 / the fine fraction are used interchangeably throughout this thesis).

Figure 2.3 illustrates the Partisol in situ and its configuration. The inlet head was cleaned approximately once a month. The unit has a filter exchange and storage system which allows it to store up to 16 samples of each size fraction between site visits. The storage magazines in the machine are covered to prevent contamination during sampling.

*Figure 2.3* *Partisol dichotomous sampler in situ at Acton Town Hall (2001 – 2002) and its configuration*



It was decided that there should be a short trial period at the start of 2001 to determine whether quartz or Teflon filters would be most suitable for this analysis. Each type of filter has both advantages and disadvantages. PTFE is the more traditional filter substrate used for mass concentration analysis and ion chromatography whilst quartz filters can withstand high temperatures and are therefore particularly suitable for carbon analysis using thermal-optical methods or Gas Chromatography/Mass Spectrometry. It was important not to 'lock-out' any types of possible analysis at the beginning of the sampling campaign. Both types of filter are likely to have both positive and negative artefacts associated with them. The trial period started with Teflon filters and sampling began on 12 January 2001. However, on 17 January 2001 there was a high particulate episode which led to a flow error occurring on the machine. When this type of error occurs on a Partisol the default setting is for the machine to shut down and carry out no further monitoring until reset. The next site visit did not occur until 19 January and three days monitoring was lost. The default setting was changed so that the machine would continue monitoring with new filters from midnight should a flow error re-occur. The same problem re-occurred on 21 January. It seemed likely that flow errors would continue to be a problem if Teflon filters were used and sampling with quartz filters (Whatman, Brentford, UK) started on 10 February 2001.

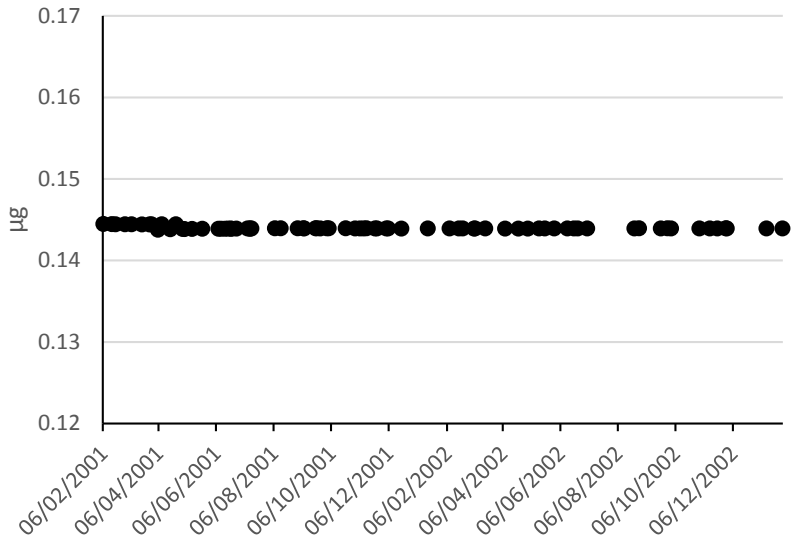
The problems with the Partisol itself were not entirely resolved with the change of filter substrate. Errors also occurred with the filter exchange mechanism which would shut the machine down until reset. Harrison et al. (2004) also report similar problems with a dichotomous sampler of the same type leading to a reduction in the number of samples obtained. In addition, there was no-one available at the study site to check the machine on a regular basis. It is theoretically possible to set up a communication link between these machines and a remote location so that monitoring could be checked without a site visit and faults identified immediately. Such a link was attempted between the machine and the laboratory in central London. Unfortunately, this attempt resulted in the loss of the motherboard on the machine. Two months complete sampling was lost (December 2001 and January 2002) whilst a new motherboard was shipped over from America and installed. Occasionally sampling days were lost for other reasons, for example on 5 March 2001 access to the sampler was not allowed because it was the site of a murder scene under investigation.

The filter conditioning, weighing and storage protocols used both before and after exposure followed the guidance set out in LAQM Technical Guidance TG (09).

Prior to exposure the quartz filters were baked at a temperature of at least 600 ºC for approximately 2 hours to remove organic contamination. There were a number of suggested protocols available (see for example, Cachier et al., 1989 and Chow et al., 1993). The protocol used was chosen to ensure contamination removal without compromising the filter substrate. Each filter was then allocated to an individual Petri slide and left to equilibrate in a dust-free cabinet for at least 48 hours in a climate-controlled laboratory with temperature and humidity controls (20ºC (± 1ºC) and 50%RH (± 5%)). 6 blank control filters (which had also been pre-baked as above) were also left with the unexposed filters to equilibrate and were used to identify whether any changes in laboratory conditions had occurred.

Filter weighing occurred on 76 different days between February 2001 and January 2003 in the laboratory. Each filter was weighed three times on a Mettler AE 240 5 figure (0.01 milligrams) balance and the mean weight calculated. The balance was 're-zeroed' between each weighing. At the start of each weighing session the control filters were each weighed three times. A check was made against previous weighings of these filters to check whether there had been any significant changes. Figure 2.4 demonstrates that no significant change occurred in mean weight of the control filters during the study period.

*Figure 2.4* *mean weight of six blank quartz filters used as laboratory controls (February 2001 to January 2003)*



After weighing, the sample filters were each allocated a unique number and placed in filter holders ready for transport to the site. Each of these filter holders had a further unique identity number and a record was made of the corresponding filter to ensure that there was no confusion in relation to the identity of a filter once it had been exposed. The filter holders were placed in sequence in the filter cassette magazines and taken to the site within 24 hours. Site visits took place every 10 days or so.

At each site visit, a note was made of the actual 24 hour volume flows for each exposure period and the filter cassettes containing the exposed filters were removed and immediately returned to the laboratory. It is a strength of this study that site visits were made at the same time of day and filters were transported directly between the study site and the laboratory with minimum delay and maximum care.

In the laboratory the exposed filters were returned to their allocated Petri slides which were labelled to indicate exposure date and size fraction. The exposed filters were left in the dust-free cabinet for a further 72 hours to equilibrate and weighed on the same balance as the pre-exposure filters. The control filters were equilibrated and re-weighed at the same time. After weighing the filters were stored, in their individual Petri slides within a sealed polythene bag, at a temperature of 4$^{o}$C until subsequent analysis took place.

The deposit weight of particles on each filter was determined by subtracting the pre-exposure filter weight from the post exposure weight. An adjustment was made for small differences within the control filters' mean weight. This ranged from 0 to ±0.01%.

The mass concentration of deposit (μg $m^{-3}$) on each filter was calculated in accordance with the manufacturer's recommended method reported in their Technical Note 5 (Meyer 2001) - see Equations 1, 2 and 3. These equations acknowledged that some of the fine fraction is collected on the coarse filter and differ from those given in the manufacturer's manual originally supplied with the machine. Concentrations are reported at ambient temperature and pressure. The calculations gave mass concentrations for $PM_{2.5}$, $PM_{coarse}$ and, by combining the measurements, $PM_{10}$.

Sampling using quartz fibre filters finished on 31 December 2002 and was successful on 422 days (out of a possible 730 days).

*Equations (1), (2) and (3):*

'For *fine* PM:

$$C_f = \frac{M_f}{V_f} \qquad (1)$$

For *coarse* PM*:*

$$C_c = \frac{M_c}{V_t} - \left(\frac{V_c}{V_t}\right) C_f \qquad (2)$$

For PM-10:

$$C_t = C_f + C_c \qquad (3)$$

The symbols in equations (1), (2) and (3) represent:

$C_f$ = mass concentration [$\mu g/m^3$] of fine particle fraction

$C_c$ = mass concentration [$\mu g/m^3$] of coarse particle fraction

$C_t$ = mass concentration [$\mu g/m^3$] of PM10

$M_f$ = mass [$\mu g$] collected on fine particle fraction filter

$M_c$ = mass [$\mu g$] collected on coarse particle fraction filter

$V_f$ = volume [$m^3$] of air sampled through *fine* particle fraction filter

$V_c$ = volume [$m^3$] of air sampled through *coarse* particle fraction filter

$V_t$ = total volume [$m^3$] of air sampled through *both* fine and coarse particle fraction filters (total volume)

## PM sampling at Marylebone Road and North Kensington 2002 – 2012 and Oxford Street 2011 - 2012

Publicly available PM10 and PM2.5 mass concentrations from Partisol 2025 samplers located at Marylebone Road and North Kensington between 2002 and 2012 are used in this research project. There is only limited data for 2007 and 2008 available and these two years do not form part of this study. The filter medium used as the collection substrate between 2002 and 2006 was quartz. This was changed to Emfab™ in 2007 following an investigation which concluded that the quartz filters provided an over-estimation of PM mass concentrations (Maggs et al., 2008). Details of the sampling programmes are set out in a series of annual reports (see for example, Beccaceci et al., 2013). The mass concentration of PM on each filter was calculated in accordance with the manufacturer's recommended method as set out in Equation 4.

*Equation 4*

$$MC = \frac{DW \times 10^6}{V}$$

where:

DW = net change in mass (g) of the 47 mm filter between the initial weighing and the post-collection weighing

$10^6$ = conversion factor from grams (g) to micrograms (μg).

V = the volume drawn through the filter, as obtained from the sampler (actual volume).

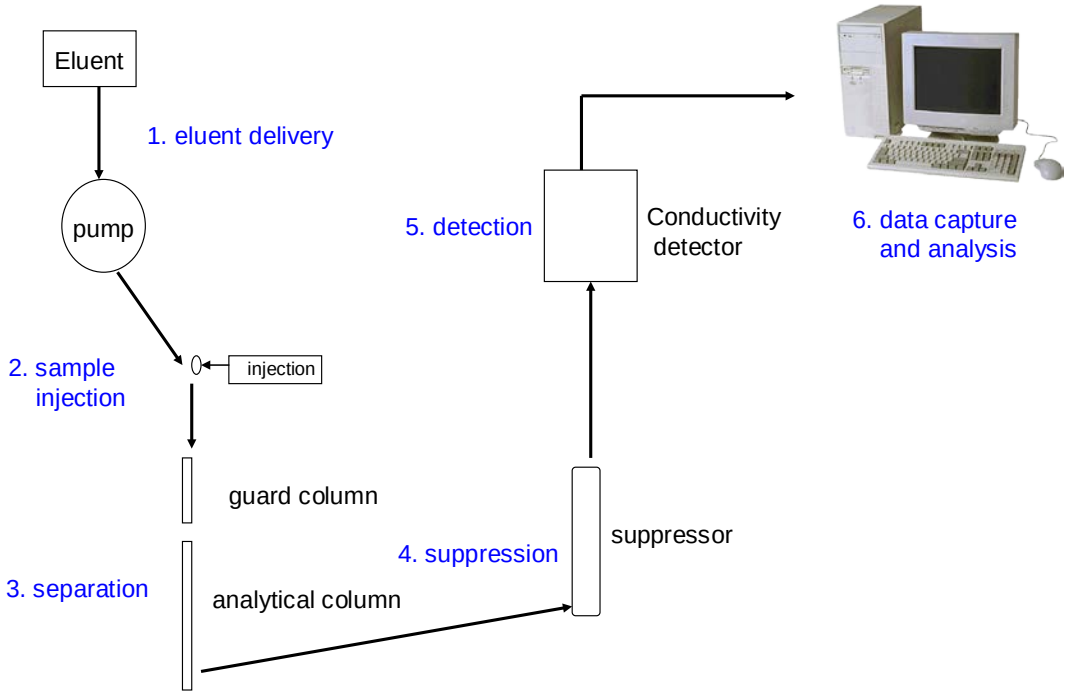
PM10 sampling at Oxford Street in central London was carried out by ERG at KCL on behalf of Westminster City Council as part of the London Air Quality Network using Emfab™ filters and a Partisol 2025 sampler. The protocols and QA/QC for these measurements are as described above. Mass concentrations were reported via the Londonair website. Filters from these sampling programmes are archived at KCL. The filters from North Kensington were not available for further analysis as they were used for metal analysis.

# Analysis by ion chromatography

## Acton Town Hall

Figure 2.5 is a schematic diagram of the ion chromatograph process. Basically there are six stages. A sample is injected into an eleunt stream and pumped through an ion exchange column. The different ions in the solution are separated in the column in accordance with their molecular weight and valence of the ion. The higher molecular weights are more strongly held on the column and therefore the lighter charged ions are eluted first and detected by the electrical conductivity detector. The final stage is data capture and analysis resulting in the production of a chromatogram and concentration measurements based on peak area.

*Figure 2.5* *ion chromatography – general schematic diagram*



All the whole filters were equilibrated in the dust free cabinet for at least 48 hours with the control filters and then all the filters re-weighed. A check was made against the original weight to ensure that there had been no change in mass during storage. The filter was then cut in half (approximately) using a clean scalpel. The half filter for analysis was reweighed three times and a mean weight taken. The unused half filter was returned to storage at 4°C. Ten blank pre-baked filters were also subjected to the same procedure to test for any pre - contamination by any of the analytes.

A half filter has been shown to be representative of the whole by Zhou (1997) and Stribley (2004). Harrison et al (2004) similarly analysed half filters collected contemporaneously with this study. The practice of using half filters has since become established and has been used by, for example Hayman et al. (2008) on behalf of Defra. Indeed Harrison and Yin (2010) analysed only "a piece" of a quartz fibre filters for ion chromatography analysis. These studies represent a range of monitoring sites and no site-specific problems have been identified in any of these studies.

Each half filter was soaked in 5 ml of de-ionised distilled water in a new plastic (stoppered) tube and sonicated in a bath for at least 30 minutes. Plastic rather than glass tubes were used as they had been shown by Stribley (2004) not to give any anion contribution. The use of de-ionised distilled water was to ensure the best analytical results without contaminants from the water supply. There was one exception to the procedure adopted by Zhou (1997) and Stribley (2004) in that they squirted ethanol on the filter prior to soaking to loosen the particulate 'cake' on the filter due to the hygrophobic nature of the PTFE filter substrate. Using ethanol on a quartz filter simply resulted in the ethanol being absorbed into the filter at the point of application and not across the whole filter. It was decided that the nature of the substrate was such that additional sonification should ensure that the anions entered into suspension and therefore each filter was sonicated for at least twice the amount of time recommended by Zhou (1997) and Stribley (2004). After sonication, the tubes were left overnight in the dust free cabinet and then centrifuged for 30 minutes. 2.5 ml of the clear solution was drawn off by syringe and transferred to a 5ml vial.

A Dionex Model 500 ('the Dionex') (now part of Thermo-Scientific) was used for this analysis. The eluent used in the Dionex, a mixture of 3.5 mM sodium carbonate/1 mM sodium bicarbonate as recommended by the manufacturer for this type of analysis, was de-aerated immediately before use by placing it under laboratory vacuum whilst at the same time sonicating for 30 minutes. In this way air bubbles in the columns would be avoided. The eluent was delivered to the Dionex via two parallel 1 litre bottles pressured at 6 psig air.

The eluent stock concentrate was made by dissolving 52.98 g of $Na_2CO_3$ 0.5 M and 42 g of $NaHCO_3$ 0.5 M each in two separate 800 ml of double distilled water and separately made up to 1 litre. The concentrates were then stored at 4°C. Fresh eluent was prepared for each 'run' (in this context a 'run' means a complete cycle using the Dionex and each 'run' may consist of up to 60 individual samples) by pipetting 15 ml of 0.5 M $Na_2CO_3$ and 4 ml of 0.5M $NaHCO_3$ in to a 2 litre volumetric and made up to 2 litres with double distilled water.

Standard solutions of chloride, nitrate and sulphate (i.e. the anions for analysis) were made up following a procedure set out in '*The Determination of Anions, Cations, Transition Metals, Other Complex Ions and Organic Acids and Bases in Water*' (HMSO 1990). 1000 ppm stock solutions were prepared using the quantities of 'Analar' chemicals indicated in Table 2.1 and dried in an oven at the temperature and duration shown in the table. Thereafter the salts were placed in a dessicator until cool.

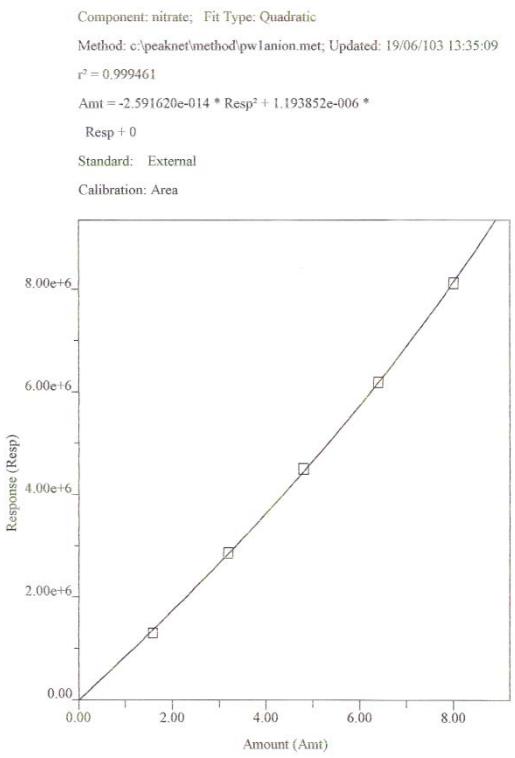
*Table 2.1 quantities of 'Analar' chemicals used to make up stock solutions for use in ion chromatography*

| **Anion (salt)** | **Amount (in 1 litre) (g)** | **Baked at temp ($^0$C)** | **Duration (hrs)** |
|---|---|---|---|
| **Sulphate ($Na_2SO_4$)** | 1.4790 | 105 | 1 |
| **Nitrate ($NaNO_3$)** | 1.3707 | 105 | 24 |
| **Chloride (NaCl)** | 1.6484 | 150 | 2 |

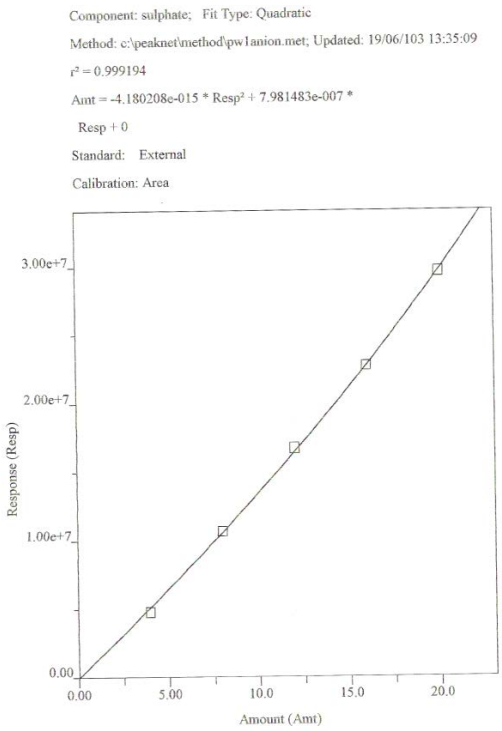
A mixed standard solution was made up from the stock solution and used for 4 'runs' before renewing. Stribley (2004) has shown that these dilute solutions may be kept for several months without any deterioration if stored at a temperature of approximately 4°C. The stock solution was therefore always stored at 4°C.

At the start of each 'run' the instrument was calibrated with a five point calibration curve, after the column had been flushed with 6 distilled water samples. The concentrations of the mixed standards were entered into the program and the installed software automatically calibrated the machine. Figure 2.6 is an example of typical calibration curves. An $r^2$ of more than 99.5% was always obtained. After every 10 samples a mixed standard sample and a distilled water sample were included to check for instrument drift and ensure the retention times remained the same.

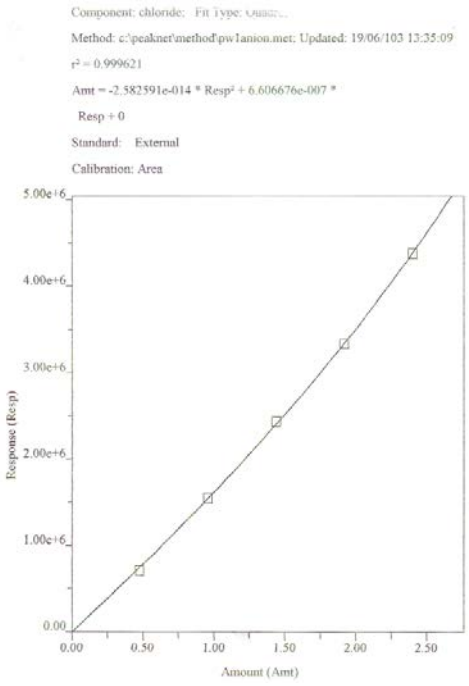
*Figure 2.6* *Dionex calibration curves for nitrate, sulphate and chloride obtained from 5 different concentrations of the mixed standard on 19 June 2003*




nitrate




sulphate




chloride

The retention times of each of these mixed standards was entered into the software and the program was then able to identify and measure the named peaks in each individual chromatogram using the regression equation.

Other peaks would be measured but not identified. Figure 2.7 are anion chromatograms of the fine and coarse filters obtained on Tuesday 10 April 2001. Peaks numbered 2, 3 and 5 on both types of filter were measured for this analysis. Peaks 1 (probably fluoride) and 4 (phosphate) were not included as part of the measurement regime.

The amount of mass (ppm) of each of the anions, chloride, nitrate, sulphate, on the half filter was determined, multiplied by the percentage filter used to calculate a whole filter concentration and then converted to $\mu g\ m^{-3}$. There was found to be a small but consistent amount of contamination by each of the analytes on the blank filters and the whole filter concentration was reduced by 0.2 ppm in respect of chloride, 0.2 ppm in respect of nitrate and 0.5 ppm in respect of sulphate to take account of this contamination.

808 filters (i.e. 404 sample days out of a possible 422) were successfully analysed for these anions. No separate cation measurements were made.

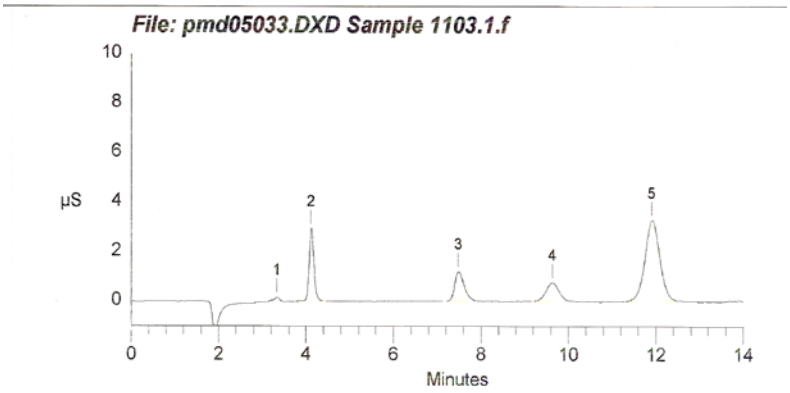
Sulphate in both the fine and coarse fractions was converted to ammonium sulphate (*1.38) because sulphate is normally neutralised to ammonium sulphate by ammonia. Similarly nitrate in the fine fraction was converted to ammonium nitrate (*1.29). Nitrate in the coarse fraction was converted to sodium nitrate (*1.37). Chloride on the coarse filter was converted to sodium chloride (*1.65). No adjustment was made in respect of the chloride in the fine fraction.

In order to compare with measurements at other sites (see next section), the nitrate found in both the fine and coarse mode was converted to ammonium nitrate (*1.29). Similarly all the chloride was converted to sodium chloride (*1.65) for comparison purposes.

*Figure 2.7 anion chromatograms obtained on 10 April 2001, Acton Town Hall*

Tuesday 10 April 2001
Acton Town Hall

Fine filter

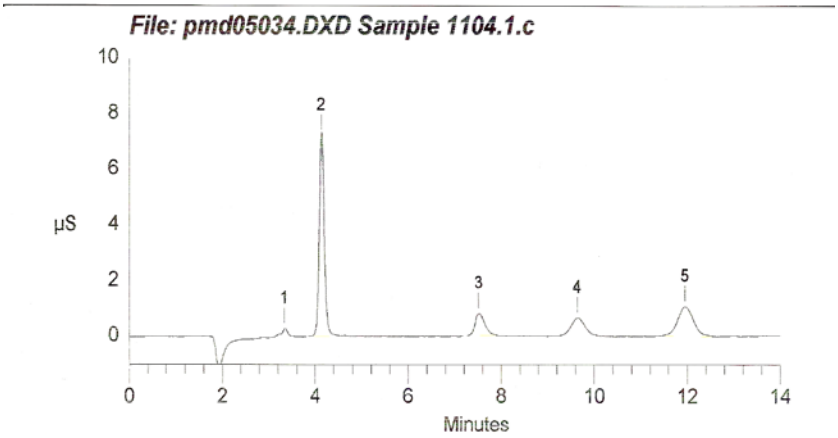



Total $PM_{2.5}$ 14.5 µg $m^{-3}$

Peak number 2 - chloride (0.7 µg $m^{-3}$)
Peak number 3 – nitrate (0.9 µg $m^{-3}$)
Peak number 5 – sulphate (2.4 µg $m^{-3}$)

Tuesday 10 April 2001
Acton Town Hall

Coarse filter




Total $PM_{coarse}$ 8.5 µg $m^{-3}$

Peak number 2 - chloride (1.2 µg $m^{-3}$)
Peak number 3 – nitrate (0.5 µg $m^{-3}$)
Peak number 5 – sulphate (0.6 µg $m^{-3}$)

# IC analysis of samples from Marylebone Road and North Kensington

At Marylebone Road and North Kensington ion chromatography measurements of sulphate, nitrate and chloride have been made as part of Defra contract CPEA 28 – 'UK Airborne Particulate Concentrations and Numbers'. Between 2001 and May 2005 the contract was awarded to Casella Stanger (now Bureau Veritas) and the samples were collected using a Partisol 2025 sampler and Teflon filters. From June 2005 the contract has been carried out by NPL and the filter substrate was changed to Emfab to avoid 'clogging' which occurred on the Teflon filters. In October 2007 the filter substrate was further changed to quartz to allow for EC/OC analysis on half filters (Hayman et al., 2008). Summaries of the sampling campaigns are set out in a series of annual reports (see for example Beccaceci et al., 2013). No $PM_{10}$ mass concentration measurements were made of the samples collected on the filters used for the IC analysis.

The measurements of sulphate, nitrate and chloride anions extracted from these datasets have been converted to measurements of concentrations of ammonium sulphate, ammonium nitrate and sodium chloride as set out in the previous section.

# Retrospective Carbon analysis

Measuring particulate carbon present in the atmosphere as a result of the incomplete combustion of fossil fuels is a useful method for assessing the impact of traffic emissions on air quality. However, to carry out a comparison of changes in traffic emissions which may have occurred over time it is necessary to have a time series of atmospheric carbon measurements but, other than black smoke measurements, no publicly available measurements were available from sites in London before 2007.

As discussed in chapter 1 there are a number of methods which seek to identify this atmospheric carbon, either as elemental carbon (EC) or black carbon (BC), based on the light absorbing properties of carbon. In this project a Magee OT-21 transmissometer and an EEL (Evans Electroselenium Ltd) model 43 (analogue) were chosen to provide a time series of comparative measurements of the light absorption by carbon on archived filters (at KCL) collected using Partisol 2025 samplers in the following campaigns

- Acton Town Hall 2001 – 2002,
- North Kensington 2003 – 2005,
- Marylebone Road 2003 – 2005,
- Marylebone Road 2010 to 2012, and
- Oxford Street 2011 - 2012

A distinct advantage of both of these measurement methods is that the sample is not destroyed in the process and is available for further analysis if required. No standard conversion algorithms are available to provide equivalent BC (EBC) concentrations from these measurements and the initial aim of this analysis was to identify an equation which would provide comparative EBC concentrations at each of the sample sites. Elemental carbon analysis of a selection of filters was obtained by the IMPROVE-TOR method for 100 fine fraction filters (quartz) from Acton Town Hall and the NIOSH-TOT method in respect of quartz filters from Marylebone Road and North Kensington. A description of these methods is provided below. Daily publicly available elemental carbon measurements

from Marylebone Road between 2010 and 2012 were used together with filters analysed for EC by the same method collected at both of these sites between 2003 and 2005. EC has been chosen as the more appropriate parameter in this study because it is derived from time resolved samples all of which, in this project, were collected using a Partisol sampler. BC measurements obtained from real-time aethalometer measurements were also available from Marylebone Road from October 2006 and North Kensington from November 2008 as part of the revised Black Carbon Network.

Details of the analytical methods are given in the following sections.

## Transmissometry

The Sootscan ™ Model OT21 Transmissometer ('transmissometer') – see Figure 2.8 - has been developed by Magee Scientific (Berkeley, California, USA) as a laboratory based equivalent of the Magee aethalometer deployed at a number of locations in London and elsewhere providing real-time measurements of Black Carbon. The transmissometer provides a simple, non-destructive analysis of filter samples. Magee Scientific (www.mageesci.com) point out that sample analysis may be performed on archived filters as well as freshly collected ones. The transmissometer measures the absorption of light by particles collected on a filter at two wavelengths: 880 nm and 370 nm. The measurements at 880 nm, in the infrared spectrum, are interpreted as black or elemental carbon as only carbon absorbs light at this wavelength. The measurements in the ultraviolet spectrum at 370 nm are, according to Magee Scientific, an indicator of aromatic organic compounds such as wood smoke.

The transmissometer was operated in accordance with the Operator Manual (2007). The machine was calibrated to blank filters of the appropriate substrate (in this case, either quartz or Emfab). At the start of each new batch of analysis the calibration of the machine was checked by placing (using forceps) blank filters of the appropriate substrate in both trays in the filter holder. The machine is linked via software to a personal computer and measurements are outputted to the computer as a csv.file which may then be imported into spreadsheet programs such as Microsoft Excel. Thereafter, a blank filter of the appropriate

substrate was placed in the rear tray of the filter holder as a blank reference filter and the sample filter was placed in the front tray. Neutral Density Film was also available. This was placed over a blank filter and used after every 15 samples or so during each session to ensure that there was no drift in the measurements. UV and IR attenuation was calculated as:

$$ATTENUATION = 100 * \ln Io/I \text{ (blank filter light transmission/ sample filter light transmission)}$$

Whole Emfab filters from Marylebone Road and Oxford Street were analysed by this method. Only half filters (quartz) were available from the sampling campaign at Acton Town Hall as IC analysis had already taken place. Adaptors for the filter tray are available and 25 mm punches were taken from the fine filters and analysed. By analysing 5 whole filters that had been exposed but not used for IC and then taking these smaller punches it was found that there was a small but consistent over-estimation of the attenuation on each filter of 5±0.5 ATN units. 5 ATN units were therefore deducted from each filter measurement before any further analysis took place.

To provide a time series, the results of analysis of quartz filters from previous sampling campaigns at Marylebone Road and North Kensington between 2003 and 2005 and during 2010 (n = 103) were also utilised (Sweeney, 2008 and Tremper et al., 2013). These measurements were carried out using the same transmissometer and the method described above.

Whilst both ultraviolet and infrared measurements are determined by transmissometry, only the infrared (λ 880 nm) measurements (ATN IR) have been used in this project as it is the equivalent black carbon component which is of interest.

*Figure 2.8 The Sootscan ™ Model OT21 Transmissometer ('transmissometer')*


*Photograph courtesy of Magee Scientific (www.mageesci.com)*

# Reflectometry

All the filters measured using the transmissometer (other than those which were used to determine an EC calibration) were also measured using the EEL (Evans Electroselenium Ltd) –model 43 (analogue) see Figure 2.9 - following the procedure set out in Chapter 7 ('Assessment of Smoke Stains') of the 'UK Smoke and Sulphur Dioxide Network Instruction Manual' (DETR, 1999). The EEL 43, which was traditionally used to measure the stain on filter for the black smoke network, consists of a tungsten lamp and photo-sensitive selenium disc. The same reflectometer was used for all of the analysis in this project and the work was essentially carried out in two tranches. However, there was a substantial time lapse between each period of use. To ensure consistency of results the machine was serviced and re-calibrated by Kemtronix Ltd (Newbury, Berkshire, UK) before each analytical period.

At the start of each analysis session, the EEL reflectometer was calibrated according to the manufacturer's instructions using a white and grey tile provided with the machine. Once calibrated against these, a blank filter of the same substrate (in this study either quartz or Emfab$^{TM}$) as the filter sample was placed under the measuring head and the machine set to '100' (i.e. no light absorption). The reflectance of each filter was then measured by placing the sample filter on the white tile and at least three measurements taken at random locations across the exposed part of the filter. Determination of a reflectance value (R) was made by reading the dial measurement (1 – 100 units) on the analogue machine. The mean of these measurements was taken. The calibration of the machine was checked every 8 – 10 filters using the blank filter and if necessary re-set to 100. If there had been any significant machine drift such that the reading before re-setting was ± 3% then repeat measurements of the previous filters were made. This was not a common occurrence. After each measurement the mask was cleaned with de-ionised water to prevent cross-contamination. Between readings the measuring head and mask were placed on a dark surface (matt black cartridge paper) as advised in the handbook. Hammonds (2012) operated a similar instrument in a dark corner of the laboratory but this was not possible in this analysis. However, the lighting was always consistent within the area of laboratory used for the analysis.

Light absorption was expressed as ln(Ro/R) where

$R_o$ = the intensity of reflected light from the surface of the blank filter

$R$ = the intensity of reflected light from the surface of the sample filter

*Figure 2.9 EEL model 43 (analogue)*


A method for determining an equivalent black carbon (EBC) concentration from transmissometry and reflectometry measurements is developed in chapter 5.

# EC measurements

No method for analysing the concentration of carbon on filters collected at Acton Town Hall was available in the laboratory at KCL at the time of that study. 100 fine filters were sent to the Division of Atmospheric Sciences at the Desert Research Institute (DRI), Reno, NV, US for carbon analysis. To avoid, as far as possible, collecting post-sampling artefacts, the filters were shipped in protective wrapping which would maintain the samples below freezing (approximately minus 15°C) for the duration of the journey. Dillner et al. (2009) recommend avoiding warm environments for the storage of filters to prevent loss of organic carbon after sampling. At the DRI the filters were subjected to thermal/optical reflectance (TOR) analysis following the IMPROVE (Interagency Monitoring of Protected Visual Environments) protocol as outlined in the DRI Standard Operating Procedure document as revised (2000).

In summary, the method is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) at differing temperatures. A portion of the sample is heated and carbon compounds are liberated under different temperature and oxidation environments and converted to carbon dioxide ($CO_2$) which is then reduced to methane ($CH_4$). The amount of methane present is quantified by a flame ionisation detector (FID). Carbon evolving below 550°C is deemed to be OC with EC deemed to evolve at higher temperatures. A correction is made for organic carbon compounds which will have been pyrolysed to EC by monitoring changes in the reflectance of the sample using the optical component of the analyser. Without this correction elemental carbon would be over-estimated. Seven different temperature fractions (4*OC, 3*EC) plus the pyrolysis correction are determined. The analyser measures effectively between 0.05 and 760 μg carbon/$cm^2$. The filter substrate needs to be quartz because it is the only type of filter which can withstand the high temperatures utilised in this process.

A thermal- optical method, NIOSH-TOT (National Institute of Safety and Health – Thermal Optical Transmittance) has been used by Defra to analyse elemental carbon from filters collected by a Partisol 2025 located at North Kensington and Marylebone Road and a long time series of this analysis is available. The analysis method is similar to

the IMPROVE-TOR method except that the temperature at which EC is detected is different ($750^0$C) and transmission of a laser beam through the filter monitors the pyrolitic conversion rather than reflectance. Details are set out in a series of annual reports (see for example Beccaceci et al., 2013).

There is debate about the accuracy of the split between OC and EC using these methods and both methods have been the subject of much research (see for example, Chow et al., 2001, Chow et al. 2004, Chow et al., 2005 and Watson et al., 2005).

## Black Smoke Data

Black smoke data are held by ERG at KCL and are publicly available. Black smoke concentrations from Marylebone Road between 1999 and 2008 and Greenwich High Road 1990 to 2008 were used. The black smoke concentrations were converted to equivalent black carbon concentrations using an equation provided by Heal and Quincey (2012) as follows:

$$BC\ (\mu g\ m^{-3}) = (0.27 \pm 0.03) * BSI_{(British)} - (4.0 \pm 0.2) * 10^{-4} BSI_{(British)}^2$$

# Summary of Datasets

For ease of reference, Table 2.2 summarises the main datasets utilised in this research project indicating the data sources (i.e. this project, other research at KCL, or publicly available) for each site and sampling period. In addition, publicly available measurements of NOx ($NO + NO_2$) concentrations at Marylebone Road and Acton Town Hall have been used for comparative purposes, as well as daily traffic count data for Marylebone Road.

*Table 2.2 Summary of datasets used in this project and their provenance*

| Type of analysis Site | Time period | No of sample days | Data source | | |
|---|---|---|---|---|---|
| | | | This project | Other research at KCL | Publicly Available |
| **PM Mass concentration** | | | | | |
| **PM10** | | | | | |
| Acton Town Hall | 2001 – 2002 | 422 | ✓ | | |
| Marylebone Road | 2002 – 2006 | 1469 | | | ✓ |
| Marylebone Road | 2009 – 2012 | 1221 | | | ✓ |
| N Kensington | 2002 - 2006 | 1560 | | | ✓ |
| N Kensington | 2009 -2012 | 1342 | | | ✓ |
| Oxford Street | 2011 – 2012 | 553 | | | ✓ |
| **PM2.5** | | | | | |
| Acton Town Hall | 2001 – 2002 | 422 | ✓ | | |
| Marylebone Road | 2002 -2006 | 1260 | | | ✓ |
| Marylebone Road | 2009 – 2012 | 806 | | | ✓ |
| North Kensington | 2002 – 2006 | 1662 | | | ✓ |
| North Kensington | 2009 – 2012 | 1346 | | | ✓ |
| **Ion chromatography** | | | | | |
| Acton Town Hall | 2001 – 2002 | 404 | ✓ | | |
| Marylebone Road | 2002 – 2012 | 2826 | | | ✓ |
| North Kensington | 2002 – 2011 | 3118 | | | ✓ |
| **Transmissometry** | | | | | |
| Acton Town Hall | 2001 – 2002 | 273 Quartz | ✓ | | |
| Marylebone Road | 2003 – 2005 | 157 Quartz | | ✓ | |
| Marylebone Road | 2010 – 2012 | 614 Emfab<br>37 Quartz | ✓ (614) | ✓ (37) | |
| North Kensington | 2003 – 2005<br>2010 | 115 Quartz<br>35 Quartz | | ✓ | |
| Oxford Street | 2011 – 2012 | 540 Emfab | ✓ | | |
| **Reflectometry** | | | | | |
| Acton Town Hall | 2001 – 2002 | 411 | ✓ | | |
| Marylebone Road | 2003 – 2005 | 157 | ✓ | | |
| Marylebone Road | 2010 – 2012 | 614 | ✓ | | |
| North Kensington | 2003 – 2005 | 115 | ✓ | | |
| Oxford Street | 2011 – 2012 | 540 | ✓ | | |
| **Elemental Carbon** | | | | | |
| Acton Town Hall | 2001 – 2002 | 100 | ✓ | | |
| Marylebone Road and North Kensington | 2003 – 2005 | 31 | | ✓ | |
| Marylebone Road | 2010 – 2012 | 548 | | | ✓ |
| North Kensington | 2010 – 2012 | 614 | | | ✓ |
| **Black Smoke** | | | | | |
| Marylebone Road | 1999 – 2009 | 2199 | | | ✓ |
| Greenwich High Road | 1990 – 2008 | 5866 | | | ✓ |

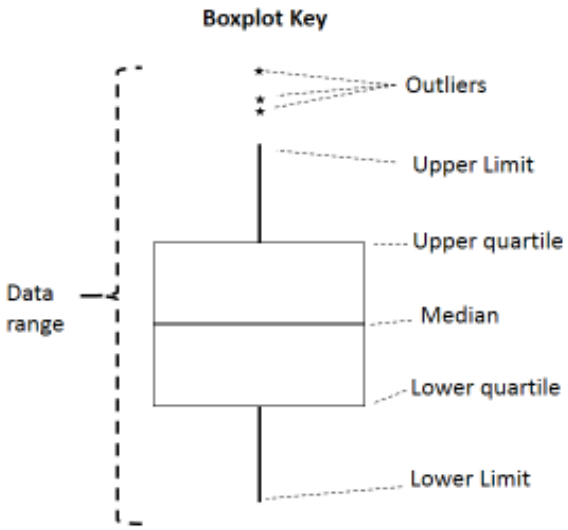
# Analysis Methods

This section describes the analysis of the datasets listed in Table 2.2 carried out to achieve the research aims and objectives of this project set out in chapter 1.

## Time series and boxplots

Each dataset is initially described by way of a time series plot generated in Microsoft Excel and a boxplot produced using Minitab v 16. Time Series plots have been used to provide an initial understanding of variation in a dataset which may be occurring over time. Boxplots illustrate the distribution of datapoints within the overall dataset and are a useful tool for identifying the main features of a dataset including outliers and for comparison with other similar datasets. An illustration and explanation of a typical boxplot is provided in Figure 2.10. In air quality studies the outliers in a boxplot, indicated with an asterisk, are particularly useful in highlighting days when concentrations of the species under consideration are elevated.

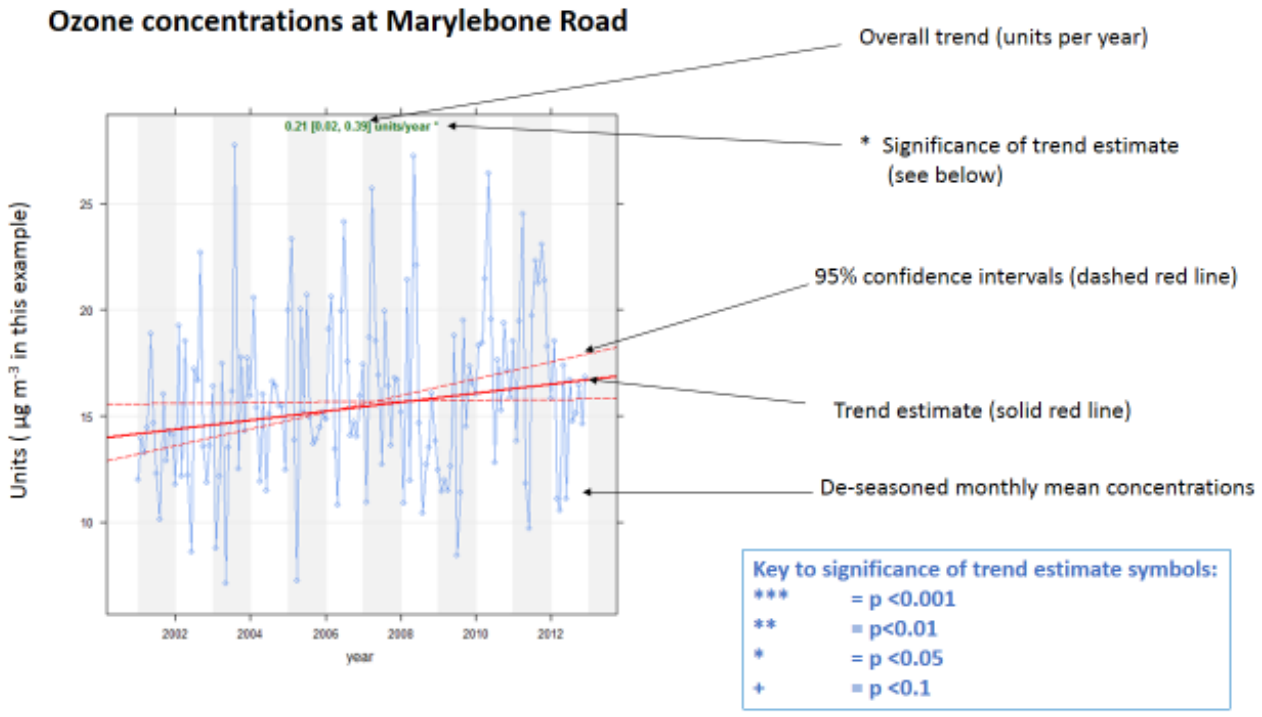
*Figure 2.10 Distribution of data within a boxplot*



# Trend analysis

Trend analysis may also be a useful tool when looking for evidence of change although needs to be treated with some caution as it may be particularly influenced by the length of the dataset, the number of datapoints within the dataset and the length of time over which data are available. Bearing these caveats in mind trend analysis has been carried out in this project using the TheilSen function in the Openair package for R software (Carslaw and Ropkins, 2012) which has been developed specifically for air quality analysis. This package is freely available for download from the Londonair website (www.londonair.co.uk) together with a manual (Carslaw, 2012). Carslaw (2012) provides useful descriptions of all the various functions within the Openair package. The TheilSen method for trend analysis was developed in the 1950's but needed sufficient computing processing power to become available to carry out all the relevant calculations. A typical plot, with explanation, is illustrated in Figure 2.11.

*Figure 2.11* *Example of a trend analysis plot (ozone at Marylebone Road) determined using the TheilSen function in Openair*



Determining variation in concentrations of any species according to the day of week is a particularly useful tool when considering whether human activity is responsible for that variation as it is only human activity which cycles over a seven day period. Day of week variation has therefore been determined using the timeVariation function in the Openair package for concentrations of each species in each dataset. In addition the timeVariation function has been used to highlight monthly variation in each species. It is possible to extract mean (arithmetic) data for each measurement using the timeVariation function but not the number of samples in each category.

In this study, vehicle count data might be useful in demonstrating that day of week variation in EBC concentrations determined in chapter 6 is similar to daily traffic flows but using overall vehicle counts may not be the most useful indicator as it is the contribution by diesel fuelled engines which is of interest when considering EBC emissions. Daily vehicle count data are available for Marylebone Road for the period studied in this thesis (i.e. from 1999 to 2012) which includes a breakdown of numbers by vehicle type and an overall vehicle volume count. During the study period there have been two methods for characterising the type of traffic:

1. Between 1999 and 2010

| | |
|---|---|
| CLS 1 | Motorbikes |
| CLS 2 | Car/Light van |
| CLS 3 | Car/Light van + trailer |
| CLS 4 | Light Goods Vehicle/ Medium Goods Vehicle |
| CLS 5 | Articulated lorry/Rigid + trailer |
| CLS 6 | Bus or coach |

2. Between 2007 and 2012

| | |
|---|---|
| CLS 7 | All vehicles up to 5.2 m in length |
| CLS 8 | All vehicles between 5.2m and 6.3m in length |
| CLS 9 | All vehicles between 6.3m and 12m in length |
| CLS 0 | All vehicles >12m in length |

Traditionally, a vehicle length of 5.2m was used to define the start of the LGV/HGV boundary at 3.5t gross vehicle weight (GVW) but this has been overtaken by changes in

design and characteristics of the UK vehicle fleet, with more than 20% of LGVs now being less than 5.2m in length but with a GVW greater than 3.5t (Transport for London, 2013). This change would have evolved gradually. Furthermore no figures are available for the ratio of private/commercial vehicles (including the proportion of cars which are taxis) or petrol/diesel fuelled vehicles within the data.

The change of vehicle classification system and vehicle design discussed above may make any consideration of day of week trends more challenging. It has therefore been decided to limit day of week analysis in relation to traffic flow to the sum of CLS 4 and CLS 5 between 1999 and 2010 and CLS 9 and 0 from 2007 on the basis that these classifications should be substantially commercial vehicles and therefore more likely to be diesel-fuelled. It should further be noted that there are some gaps within the dataset such that a breakdown of figures between these classifications is not always available and therefore only days where it is available have been used.

## Regression analysis

Within air quality studies regression analysis using ordinary least squares regression (OLS) is a useful tool when seeking to identify and/or understand the effects of change produced when variables change. An equation of the line of best fit between two or more variables may be obtained together with a correlation coefficient (r) known as the Pearson product-moment correlation coefficient, which gives an indication of the strength of association between the two variables. If perfect linearity is achieved $r=\pm1$. This would be remarkable in environmental statistical analysis but the closer the value is to $\pm1$ the stronger is the association. Significance is tested against a set of tabulated values. Squaring the coefficient ($r^2$) expresses the amount of variance in y explained by the x variable. It is important to be mindful that variation in one set of data may not necessarily caused directly by variation in the other set of data. There may be another variable upon which both variables being correlated depend.

OLS has been criticised in environmental analysis (see for example Ayers (2001) and Warton (2006)) because it assumes that all of the sampling error occurs on the y axis and the measurement on the x axis is controlled and known with confidence. Within environmental studies this is seldom the case and the two sets of measurements for comparison are both commonly from measurements taken in the field. Ayers (2001) recommends the use of Reduced Major Axis (RMA) regression analysis to replace OLS in

air quality studies because it accounts for random variation in both the x and y variable. The equation of the line of best fit is different but it returns the same correlation coefficient as OLS.

Both OLS and RMA have been used, as appropriate, in this study. OLS was carried out using Microsoft Excel (together with Minitab v16 as an additional check). The RMA regression was undertaken using an add-in designed for use with Microsoft Excel (M Sawada, University of Ottawa). However, it is a drawback of this add-in that there is no opportunity to determine an equation of the line of best fit where the intercept is expected to be zero.

## Estimating uncertainty

The accepted approach to calculate uncertainty in aggregated datasets (monthly or annual mean for example) is set out in BS ISO 11222:2002, ("Air Quality. Determination of the uncertainty of the time average of air quality measurements."), but random and non - random measurements need to be known to use this method. The publicly available datasets used here are not published with uncertainty estimates. How to minimise uncertainty by implementing consistent Quality Assurance/ Quality Control (QA/QC) and more general uncertainty estimates in relation to monitoring method and species monitored are given in the Environment Agency's Technical Guidance Note M8 (2011). More details of associated uncertainty regarding the measurements are provided in EN12341 and EN14907. For example, the expanded uncertainty of the standard measurement (i.e. gravimetric) at the daily limit value is 7.7%.

An estimate of uncertainty in this study has been provided by calculating the 95% Confidence Intervals on all the analysis but it has to be born in mind that there are associated uncertainties with the monitoring and measuring methods which will nevertheless be consistent throughout each dataset.

# Chapter 3

# Variation in $PM_{10}$ and $PM_{2.5}$ mass concentrations in London, 2001 - 2012

## Introduction

The first stage in investigating ambient particulate matter in London over the last decade is to consider overall concentrations of the regulated ambient air metrics $PM_{10}$ and $PM_{2.5}$. As set out in chapter 2, PM mass concentrations during the period 2001 to 2012 measured gravimetrically at four sites in London, namely

- Acton Town Hall, a suburban roadside site in west London,
- North Kensington, an urban background site in central London,
- Marylebone Road, a busy kerbside site in central London and
- Oxford Street, a busy shopping street in central London,

have been considered in detail.

As these locations are different source locations within London, this research will provide new insights regarding PM mass concentrations across London during the last decade.

Time series, overall trends, day of week trends and seasonal trends of $PM_{10}$ mass concentrations are reported and compared between the different locations. Compliance with regulatory requirements has also been assessed. High pollution days, defined as those where the $PM_{10}$ Daily Limit Value (DLV) of 50 $\mu g\ m^{-3}$ (as set out in EU Directive 2008/50/EC) was exceeded, have been identified and compared to other days.

$PM_{2.5}$ concentrations have been similarly quantified at Acton Town Hall, North Kensington and Marylebone Road ($PM_{2.5}$ concentrations are not available from Oxford Street). Their contribution to overall $PM_{10}$ mass concentrations were determined and compared both to $PM_{10}$ concentrations and $PM_{2.5}$ concentrations at other locations.

Based on these findings, the question of whether there has been any demonstrable change in PM mass concentrations at these type of locations in London over the last decade is considered. The question of whether or not there has been a change in the influence of $PM_{2.5}$ on overall PM mass concentrations is also discussed.

Details of the field sampling campaign at Acton Town Hall carried out in 2001 and 2002 are reported in the next section. Results of $PM_{10}$ and $PM_{2.5}$ gravimetrically measured at each of the other locations are then reported and compared to the results from the campaign at Acton Town Hall and each other.

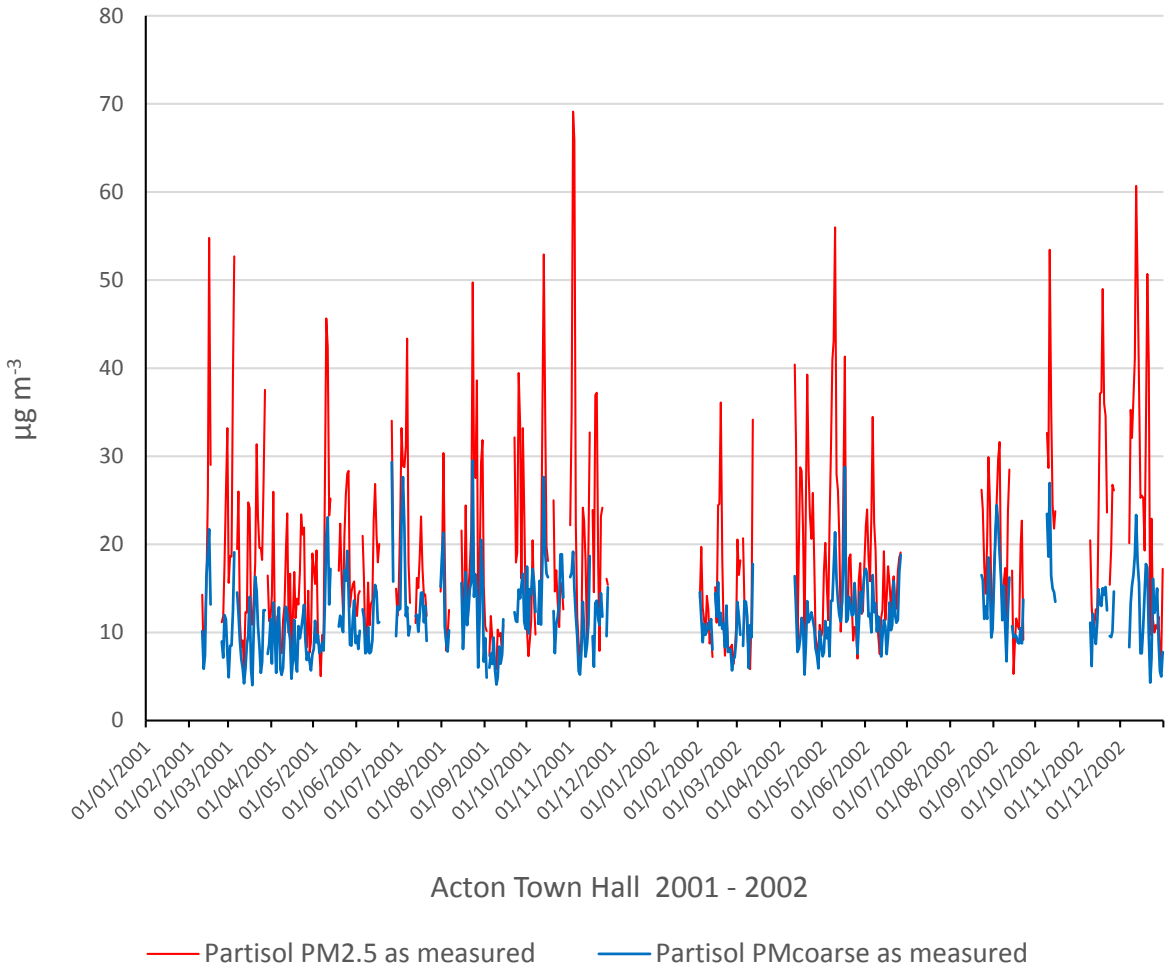
# Results and Discussion

# PM mass concentrations

## ACTON TOWN HALL 2001 – 2002

A field sampling campaign was carried out at Acton Town Hall in west London during 2001 and 2002 using a Partisol 2025 dichotomous sampler. The initial aim of the study at this site was to establish daily characteristics of the coarse and fine fractions of PM10 at a roadside site in London. At the time of the campaign, the influences of the fine fraction were poorly understood. As set out in chapter 2, the dichotomous sampler deposits were collected each day on two separate filters and PM10 mass concentrations calculated by combining the concentrations determined on each filter. For various reasons, mainly relating to mechanical problems with the Partisol itself, sampling did not occur on every day as planned. In 2001, samples were successfully obtained, using quartz fibre filters, on 236 days and in 2002 on 186 days yielding a dataset of 422 sample days. The time series of PM (coarse and fine) concentrations at Acton Town Hall, 2001 – 2002, as measured is demonstrated in Figure 3.1.

*Figure 3.1 $PM_{2.5}$ and $PM_{coarse}$ as measured at Acton Town Hall 2001 – 2002, n = 422 (Partisol 2025 dichotomous sampler)*



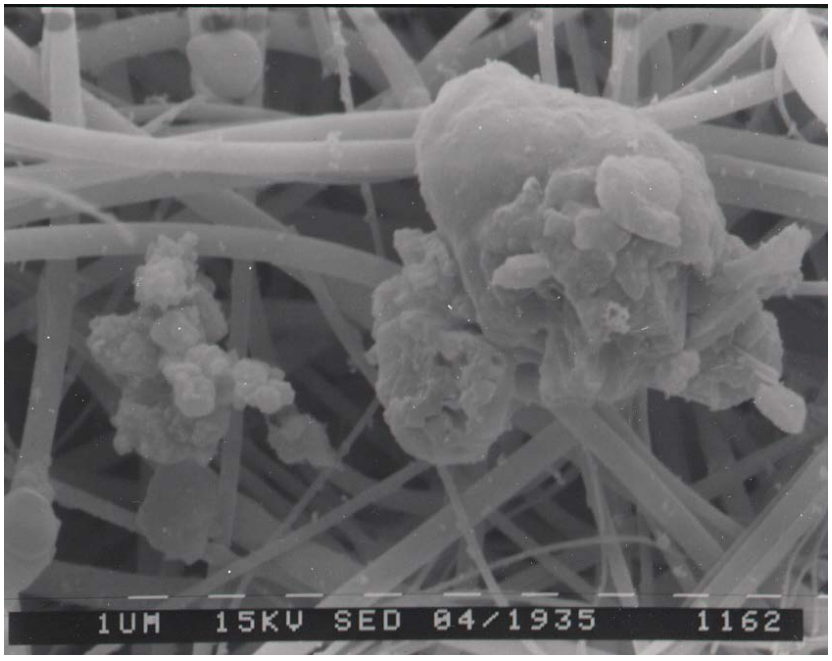
As discussed in chapter 2, when sampling with the Partisol 2025 dichotomous sampler, the filter that collected the coarse fraction also collects some of the fine fraction. Evidence for this contamination may be observed in Figures 3.2 (a) and (b) which are scanning electron micrographs, carried out by the Centre for Ultrastructural Imagining (CUI) at King's College, London (KCL), of part of the coarse and fine filters collected on 9 May 2001. The thread-like structures comprise the quartz filter substrate. Size differences between the particles on each filter were distinctive demonstrating that in general the separation of the mass between the two size fractions was successful. However, it is also clear from Figure 3.2 (b) that contamination of the coarser fraction by smaller particles has occurred. The agglomeration of particles on the fine filter is interesting. It is clearly, as an agglomeration, at about the cut-off point for $PM_{2.5}$ and perhaps the agglomeration actually happened on the filter after sampling.

The formula provided by Rupprecht and Patashnik (Meyer, 2001) to correct for this contamination (essentially approximately 11% of the fine fraction is on the coarse filter) as set out in Chapter 2 has been applied. Despite this contamination an advantage of the dichotomous sampler as acknowledged by Poor et al. (2002) is that that the separation of the particle sizes minimises the mixing of the two types of particles.

*Figure 3.2 Scanning Electron Micrograph images of filters collected at Acton Town Hall, 9 May 2001*

*(a) Fine filter*


*(b) Coarse filter (plus some fine particles)*



The descriptive statistics for each size fraction in each year are set out in Table 3.1. Figure 3.3 is the time series for the $PM_{10}$ measurements. Figure 3.4 is boxplots illustrating the distribution of each PM size fraction at Acton Town Hall. It is clear from the boxplots in Figure 3.4 that the data were not normally distributed as there were more outliers when concentrations were high. As Poor et al. (2002) and Charron et al. (2007), inter alia, point out a normal distribution is seldom achieved in these types of datasets. Geometric means would be less influenced by outlying data but have not been reported in this project because the arithmetic means are useful when comparing with other reported studies and with regulatory limits.

*Table 3.1 Mass concentrations measured using Partisol 2025 gravimetric sampler (dichotomous) Acton Town Hall – 2001 and 2002*

| | **No of sampling days** | **Arithmetic mean (95%CL)** | **Minimum (date)** | **Maximum (date)** |
|---|---|---|---|---|
| **Acton Town Hall** | | $\mu g\ m^{-3}$ | | |
| | **2001** | | | |
| **$PM_{2.5}$** | 236 | 20.9 (19.4,22.3) | 5.6 (6.5.01) | 76.8 (3.11.01) |
| **$PM_{coarse}$** | 236 | 9.6 (9.1,10.1) | 2.8 (18.3.01) | 25.6 (26.6.01) |
| **$PM_{10}$** | 236 | 30.5 (28.8,32.3) | 9.9 (9.9.01) | 88.3 (3.11.01) |
| | **2002** | | | |
| **$PM_{2.5}$** | 186 | 21.5 (19.8,23.2) | 5.9 (15.9.02) | 67.4 (12.12.02) |
| **$PM_{coarse}$** | 186 | 9.9 (9.4,10.4) | 3.2 (22.12.02) | 24.1 (17.5.02) |
| **$PM_{10}$** | 186 | 31.4 (29.4,33.3) | 12.5 (29.12.02) | 84.0 (12.12.02) |

*Figure 3.3* *PM10 mass concentrations measured at Acton Town Hall, west London, 2001 – 2002 (n = 422) (Partisol 2025 dichotomous sampler)*

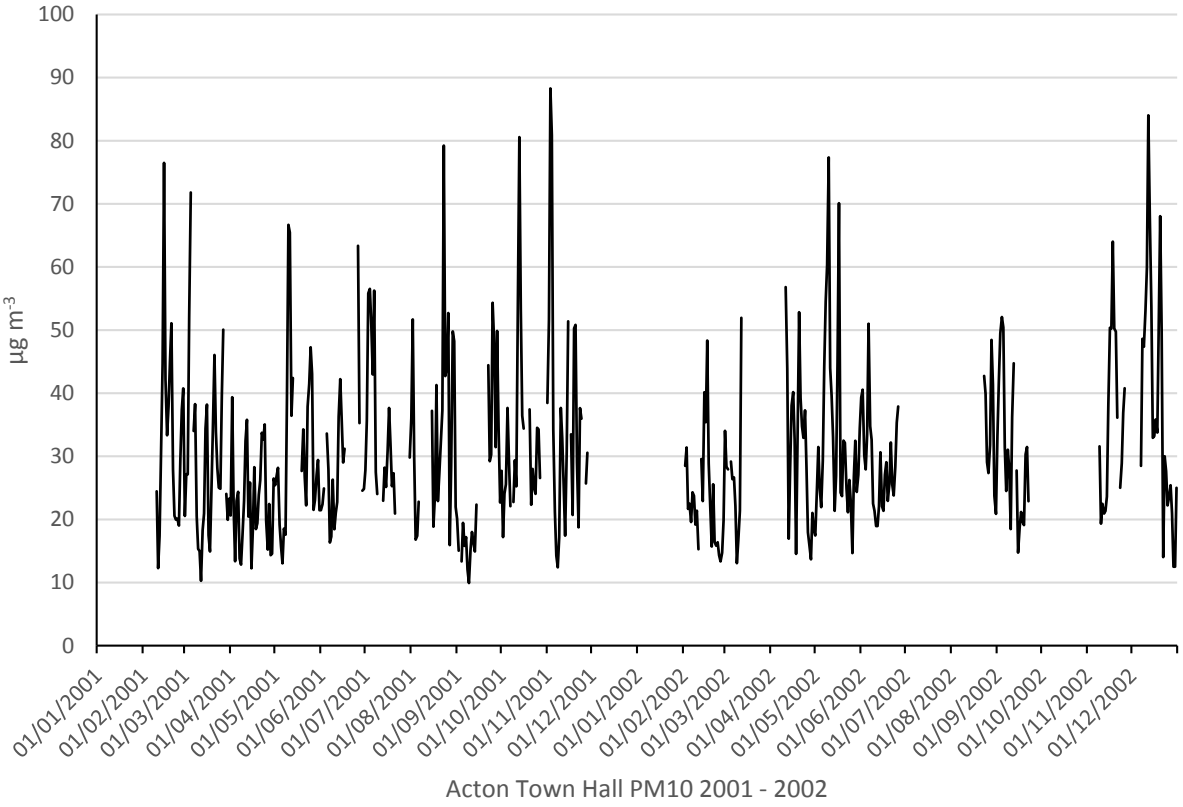
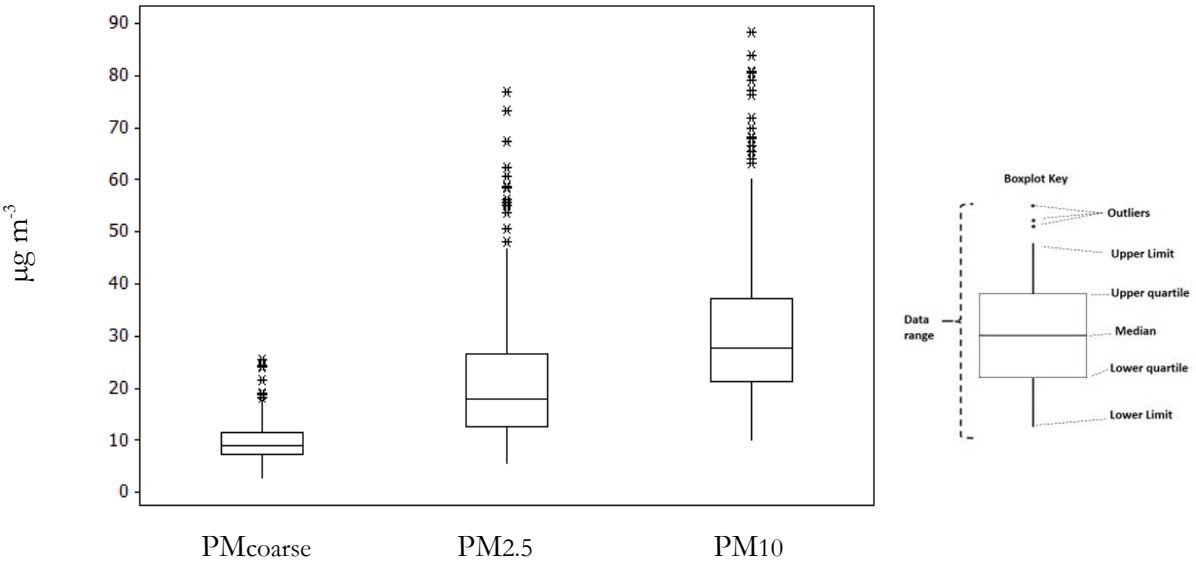



*Figure 3.4* *Boxplots illustrating distribution of PM concentrations at Acton Town Hall, 2001 - 2002*



One of the important and, at the time, distinctive advantages of carrying out this study at Acton Town Hall was that there were other co-located measurements available, including two TEOMs, one measuring $PM_{10}$ and the other measuring $PM_{2.5}$. Table 3.2 sets out the descriptive statistics for the co-located TEOMs at Acton Town Hall (a) at standard temperature and pressure with an internal correction factor and (b) at ambient temperature and pressure without the internal correction factor for comparison with gravimetric measurements as recommended by Green and Fuller (2006).

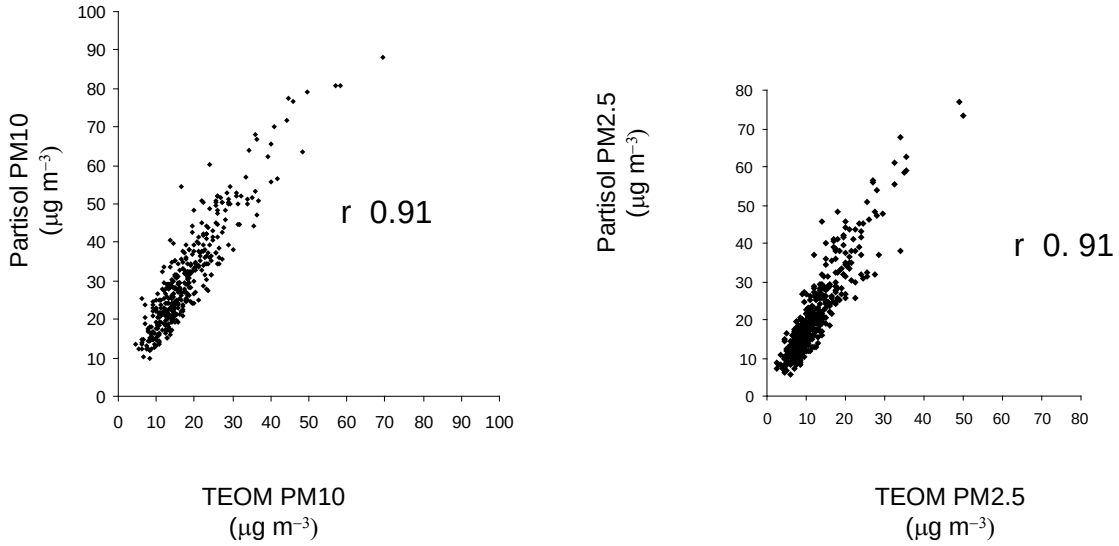
*Table 3.2* *Co-located TEOM measurements Acton Town Hall 2001 – 2002 ($PM_{10}$ and $PM_{2.5}$ sampled separately)*

| | No of sampling days | Arithmetic mean (+95%CI) | Minimum (date) | Maximum (date) |
|---|---|---|---|---|
| **Acton Town Hall 2001 - 2002** | | | | |
| **(a) Reported measurements (with internal correction factor*) at standard temperature and pressure** | | | | |
| **TEOM $PM_{10}$* ($\mu g\ m^{-3}$)** | 698 | 23.0 (22.2, 23.7) | 6.7 (1.7.02) | 69.6 (3.11.01) |
| **TEOM PM2.5* ($\mu g\ m^{-3}$)** | 722 | 16.7 (16.2, 17.2) | 5.4 (26.2.02) | 57.8 (4.11.01) |
| **(b) at ambient temperature and pressure (without internal correction factor*)** | | | | |
| **TEOM PM10 ($\mu g\ m^{-3}$)** | 689 | 18.5 (17.8,19.1) | 3.6 (1.7.02) | 69.3 (3.11.01) |
| **TEOM PM2.5 ($\mu g\ m^{-3}$)** | 709 | 12.7 (12.2,13.2) | 2.2 (26.2.02) | 49.9 (4.11.01) |

Data supplied by ERG
*Internal correction factor = 1.03 * TEOM mass + 3

The results of correlating gravimetric mass concentration data with the TEOM data are shown in Figure 3.5. Whilst there is only one Partisol gravimetric sampler the results are correlated against measurements made on the two separate TEOM samplers[5]. All instruments collect deposits which are varyingly representative of the ideal but it may be seen from Figure 3.5 that the strength of association provided by the r values (both 0.91) is very close and statistically significant ($p < 0.05$).

*Figure 3.5* *Relationship between $PM_{10}$ and $PM_{2.5}$ gravimetric measurements and same day TEOM measurements (at standard temperature and pressure), Acton Town Hall, 2001 - 2002*




The regression equations (Reduced Major Axis and Ordinary Least Squares) for the gravimetric measurements as a function of the TEOM measurements both as reported and at ambient temperature and pressure are:

RMA: Partisol $PM_{10}$ = 1.5 $T_{10(STP)}$ – 2.0 $r^2$ 84% n = 399

OLS: Partisol $PM_{10}$ = 1.3 $T_{10(STP)}$ + 0.7

RMA: Partisol $PM_{2.5}$ = 1.6 $T_{2.5(STP)}$ – 5.3 $r^2$ 85% n = 416

OLS: Partisol $PM_{2.5}$ = 1.5 $T_{2.5(STP)}$ – 3.1

T (STP) = samples measured by TEOM as reported at standard temperature and pressure (with internal correction factor)

RMA: Partisol $PM_{10}$ = 1.5 $T_{10(ATP)}$ +2.8 $r^2$ 83% n = 388

OLS: Partisol $PM_{10}$ = 1.4 $T_{10(ATP)}$ + 5.2

RMA: Partisol $PM_{2.5}$ = 1.8 $T_{2.5\,(ATP)}$ - 0.4 $r^2$ 83% n = 409

OLS: Partisol $PM_{2.5}$ = 1.6 $T_{2.5\,(ATP)}$ – 1.5

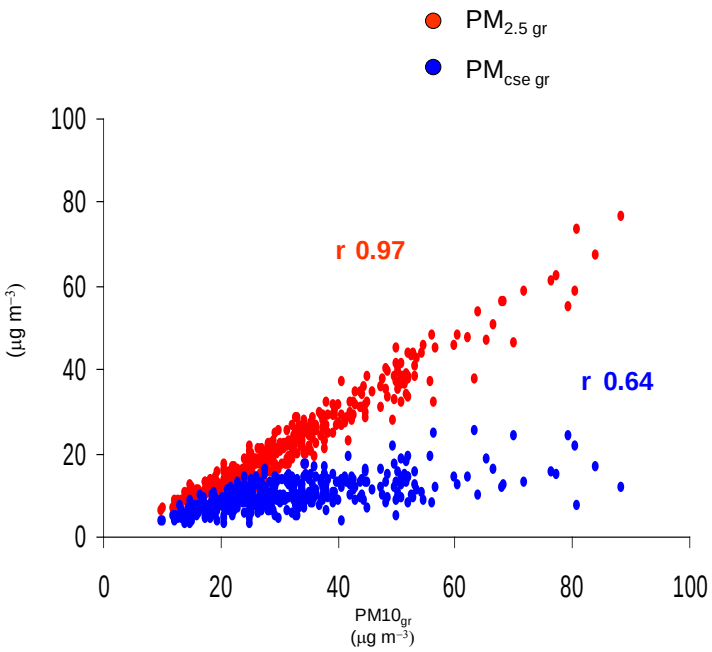
T(ATP) = samples measured by TEOM at ambient temperature and pressure

It is recognised that the TEOM instrument has poor sensitivity to volatile PM components such as ammonium nitrate, volatile organics and water (see for example Price et al., 2003 and Green et al. 2009). Given the predominance of these volatile components in the $PM_{2.5}$ fraction, it is unsurprising that greater regression gradients were obtained between gravimetric and TEOM measurements of $PM_{2.5}$ when compared with $PM_{10}$.

One of the few contemporaneous studies to consider roadside concentrations in London other than at Marylebone Road was carried out by Harrison et al., first reported in 2003, utilising a Partisol dichotomous sampler. Measurements from paired roadside and background sites located in High Holborn, Elephant and Castle and Park Lane in London were utilised together with measurements from one set of paired sites in Birmingham. They report (Harrison et al., 2004) averaged (presumed arithmetic), across all the sites, daily roadside $PM_{10}$ concentrations of 34.7 μg $m^{-3}$ and $PM_{2.5}$ concentrations of 22.3 μg$m^{-3}$ during 101 days of sampling between April 2000 and January 2002– i.e. substantially similar period to measurements at Acton. Within Europe Querol et al. (2004) report mean annual levels of roadside $PM_{10}$ concentrations ranging between 26 and 55 μg $m^{-3}$ and $PM_{2.5}$ concentrations between 13 and 39 μg $m^{-3}$. The mass measurements obtained at Acton Town Hall (Table 3.1) were within the same range as these studies giving confidence to carrying out relevant chemical speciation and other analysis.

Daily $PM_{10}$ at the study site was calculated by combining the mass concentrations of $PM_{coarse}$ and $PM_{2.5}$ measured gravimetrically with the Partisol 2025 and therefore a relationship between the size fractions and $PM_{10}$ is to be expected. There was strong daily correlation between $PM_{2.5}$ and $PM_{coarse}$ see Figure 3.6. $PM_{2.5}$ explained 94% of the variation in $PM_{10}$ demonstrating the significance of the fine fraction as the major component of $PM_{10}$ at Acton Town Hal. The coarse fraction seldom dominated total $PM_{10}$ but, whilst the correlation between the coarse fraction and overall $PM_{10}$ was not as close, it was nevertheless significant ($p \leq 0.05$) with an $r^2$ of 41% (see Figure3. 6).

*Figure 3.6 Relationship between gravimetric $PM_{2.5}$/$PM_{coarse}$ and $PM_{10}$, Acton Town Hall, 2001 - 2002*




The regression equations (Reduced Major Axis (RMA) and Ordinary Least Squares (OLS) with zero intercept) for the PM10 gravimetric measurements were:

RMA: $PM_{2.5} = 0.86\ PM_{10} - 5.28$ $r^2$ 94%

OLS: $PM_{2.5} = 0.71 PM_{10}$

RMA: $PM_{coarse} = 0.26\ PM_{10} + 1.58$ $r^2$ 41%

OLS: $PM_{coarse} = 0.29\ PM_{10}$

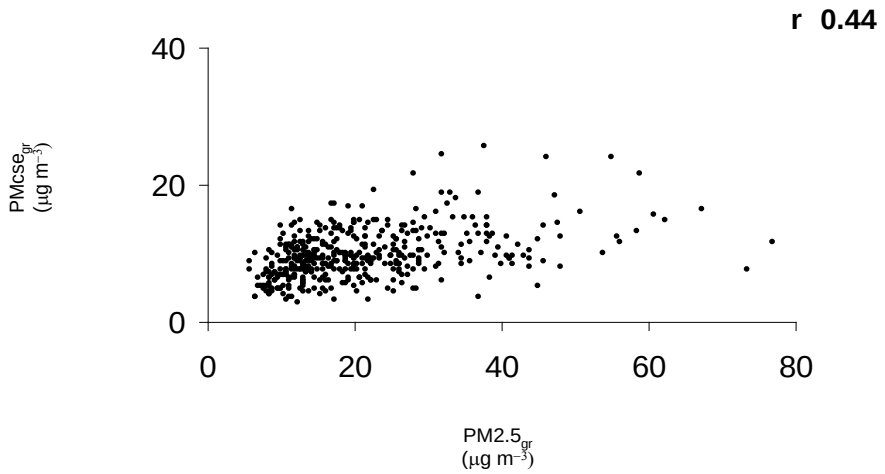
The relationship between the fine and coarse fractions, whilst statistically significant ($p \leq 0.05$), was not strong and there was a lot of scatter in the data (see Figure 3.7). Although, both fractions may increase at the same time the increase was not consistent between the size fractions indicating that different sources may influence each size fraction. The regression equations (RMA and OLS) were:

RMA: $PM_{coarse} = 0.31 PM_{2.5} + 3.21$ $r^2$ 19%.

OLS: $PM_{coarse} = 0.13 PM_{2.5} + 6.89$

The small amount of $PM_{coarse}$ related to $PM_{2.5}$ may indicate a primary component of $PM_{coarse}$ from vehicular brake and tyre wear at this roadside location being emitted contemporaneously with primary tail pipe emissions in the $PM_{2.5}$ fraction and a contribution from road abrasion being re-suspended by the passing vehicles.

*Figure 3.7 Correlation between $PM_{2.5}$ and $PM_{coarse}$ measured gravimetrically (Partisol 2025) Acton Town Hall, 2001 - 2002*



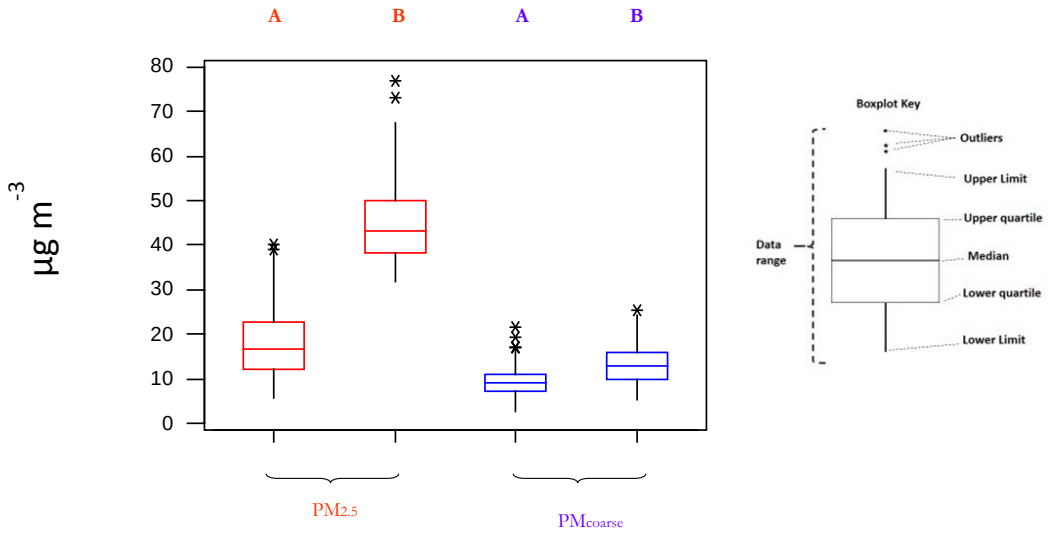
# High pollution days at Acton Town Hall

The data were disaggregated between days when $PM_{10}$ was below the daily limit value of 50 μg $m^{-3}$ (n = 374) and days when it was above (n = 48). As shown in Table 3.3, the coarse fraction mean mass was 50% greater on high pollution days ( 13.0 μg $m^{-3}$ *cf* 8.7 μg $m^{-3}$ ) but the $PM_{2.5}$ fraction mean mass was 270% greater (44.7 μg $m^{-3}$ *cf* 16.6 μg $m^{-3}$) . The contribution each size fraction makes to overall $PM_{10}$ mass concentrations also altered – see Figure 3.8.

*Table 3.3* *comparison of mean gravimetric mass of $PM_{coarse}$ and $PM_{2.5}$ (Partisol 2025 dichotomous) between days when the Daily Limit Value of 50μg $m^{-3}$ was exceeded (n= 48) and other days (n = 374)*

| | Daily mean PM10 | No of sampling days | Arithmetic mean (+95%CI) | Minimum (date) | Maximum (date) |
|---|---|---|---|---|---|
| **Partisol PMcoarse** | <50 μg $m^{-3}$ | 374 | 9.2 (8.9,9.5) | 2.8 (20.3.01) | 21.6 (3.9.02) |
| **Partisol PMcoarse** | >50 μg $m^{-3}$ | 48 | 13.8 (12.4,15.2) | 5.2 (21.12.02) | 25.6 (26.6.01) |
| **Partisol PM2.5** | <50 μg $m^{-3}$ | 374 | 18.1 (17.3,18.8) | 5.6 (6.5.01) | 40.1 (17.2.02) |
| **Partisol PM2.5** | >50 μg $m^{-3}$ | 48 | 45.7 (42.7,48.7) | 31.9 (5.7.01) | 76.8 (3.11.01) |

*Figure 3.8* *Boxplots comparing mass concentrations of $PM_{2.5}$ and $PM_{coarse}$ (measured gravimetrically) between days when the Daily Limit Value of 50µg $m^{-3}$ (n= 48) was exceeded and other days (n = 374). Acton Town Hall 2001 - 2002*




**A** **Days when Total $PM_{10}$<50µg $m^{-3}$**

**B** **Days when Total $PM_{10}$>50µg $m^{-3}$**

Comparing the days when the DLV was not exceeded in Figure 3.8 with Figure 3.4 above suggests there was no significant change to overall mass or the relative contribution made by each size fraction. It would seem that eliminating days when the DLV is exceeded might not on its own achieve overall reductions in ambient concentrations at this site. It is also clear that breaches of the EU daily limit value were largely determined by particles within the $PM_{2.5}$ fraction further guiding the source targets that might be most effectively targeted for $PM_{10}$ episode control.

The measurements of PM mass concentrations obtained at Acton Town Hall were novel at the time because of the ability to consider the contribution made by $PM_{2.5}$ and $PM_{coarse}$ to overall mass concentrations and have provided a good foundation for considering change in PM concentrations since 2002.

No further sampling with the Partisol was carried out at Acton Town Hall after 2002. Publicly available gravimetric measurements are available for the period 2001 – 2012 from the sampling sites at North Kensington, Marylebone Road and Oxford Street. Data from these sites have therefore been analysed and compared to the measurements obtained in the study carried out at Acton Town Hall.

## NORTH KENSINGTON AND MARYLEBONE ROAD, 2002 - 2012

Figures 3.9 and 3.10 are the time series graphs for gravimetric PM10 mass concentrations determined using Partisol 2025 samplers at North Kensington and Marylebone Road between 2002 and 2012. These data have been obtained from the UK Automatic Urban and Rural Network and are publicly available via both Defra's website (uk-air.defra.gov.uk) and the London Air Quality Network website (www.londonair.org.uk). It is immediately apparent that the PM10 mass concentrations reported between 2002 and 2007 are higher at both sites than those reported between 2009 and 2012 (no data were available for 2008). In May 2008 Maggs et al., on behalf of Bureau Veritas HS&E Limited, published a report entitled "Analysis of Trends in Gravimetric Particulate Mass Measurements in the United Kingdom" (Maggs et al., 2008). Maggs et al. investigated differences in reported gravimetric mass concentrations and TEOM measurements and as part of that investigation compared results of mass concentrations collected on quartz fibre and Emfab™ filter substrates. Maggs et al. (2008) reported that "the choice of filter media was shown to influence reported concentrations with quartz filters providing for an over-estimation of PM2.5 concentrations of 3.8 μg $m^{-3}$ when compared to Emfab filter measurements". It should be noted that this over-estimation was based on a comparison of 65 co-located filters. There were also discrepancies within the quartz fibre filters used such that there appeared to be two distinct types of nominally identical filters although the filters complied with the equipment manufacturer's quality criteria. It was decided that monitoring in the UK with gravimetric samplers should be changed to Emfab™ filters to reduce artefacts associated with quartz fibre filters and the changeover was made during 2007.

In this project it has been decided not to include the 2007 mass concentration data obtained at both sites for further analysis as the changeover from quartz fibre filter to Emfab™ took place during this period. It has also been decided that no trends may be inferred by looking across the whole of each dataset and the two periods (2002 – 2006 and 2009 - 2012) are therefore dealt with as two separate populations. As a number of different initiatives were introduced in 2008 (ultra -low sulphur fuel, Low Emission Zone for example) the absence of data for that year was not considered to be influential as it resulted in two distinct datasets which would be expected to provide useful comparisons.

*Figure 3.9* *PM10 mass concentrations measured at North Kensington, 2002 – 2012 (n = 3164) (Partisol 2025 sampler)*

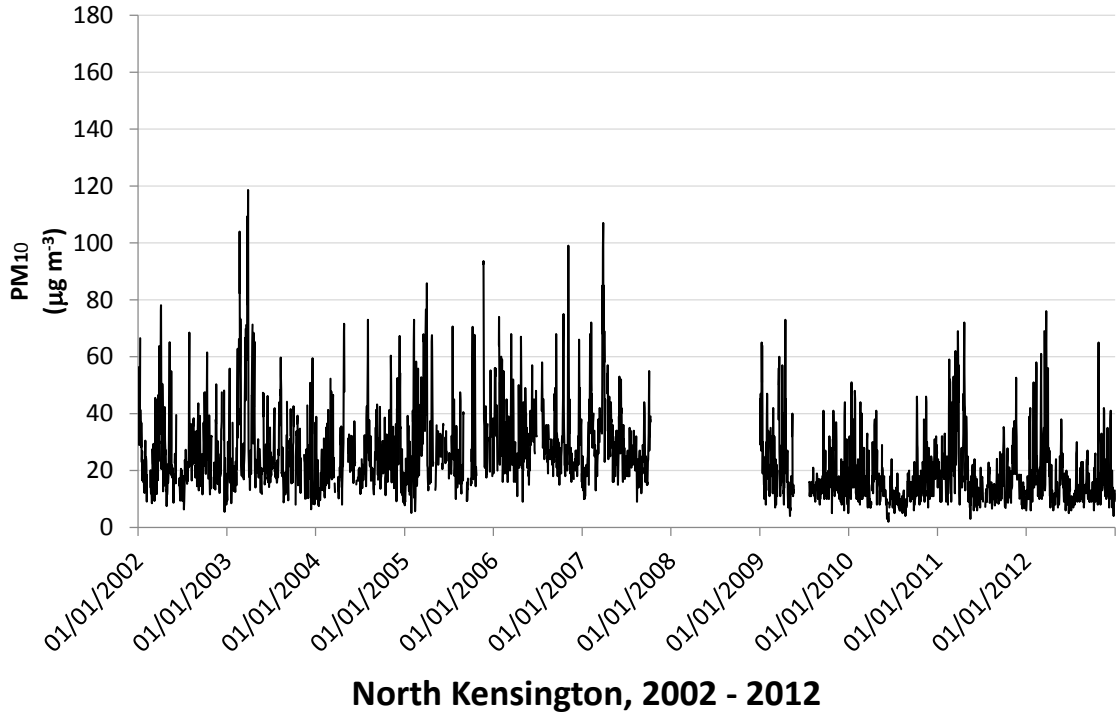
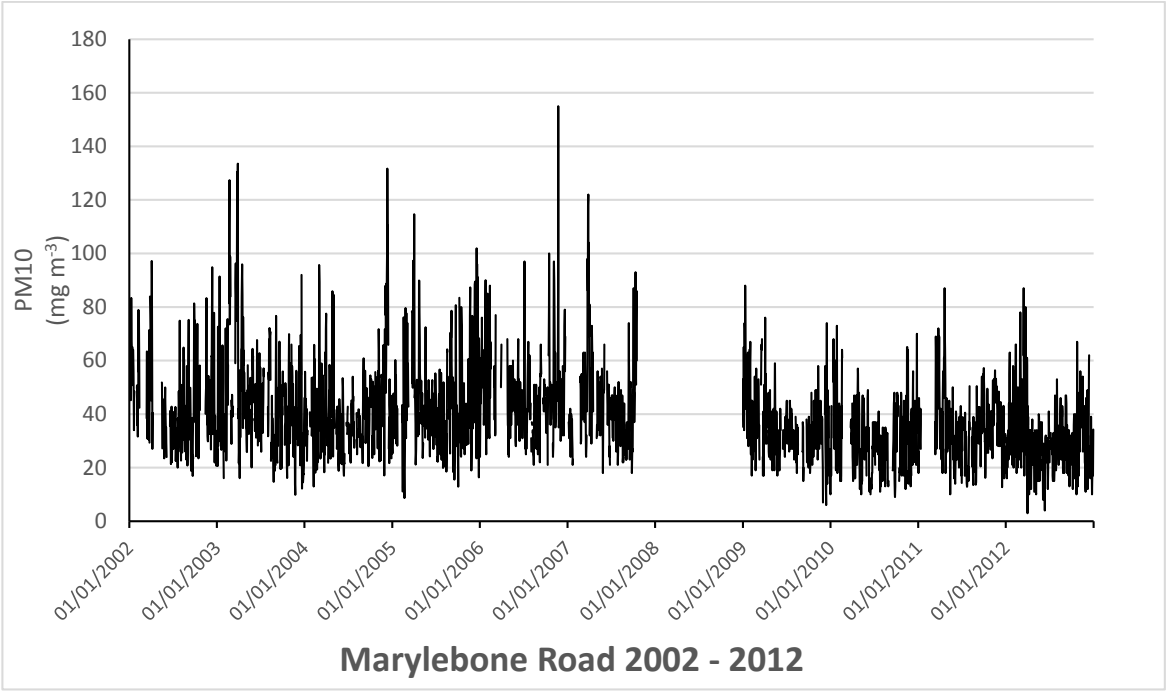


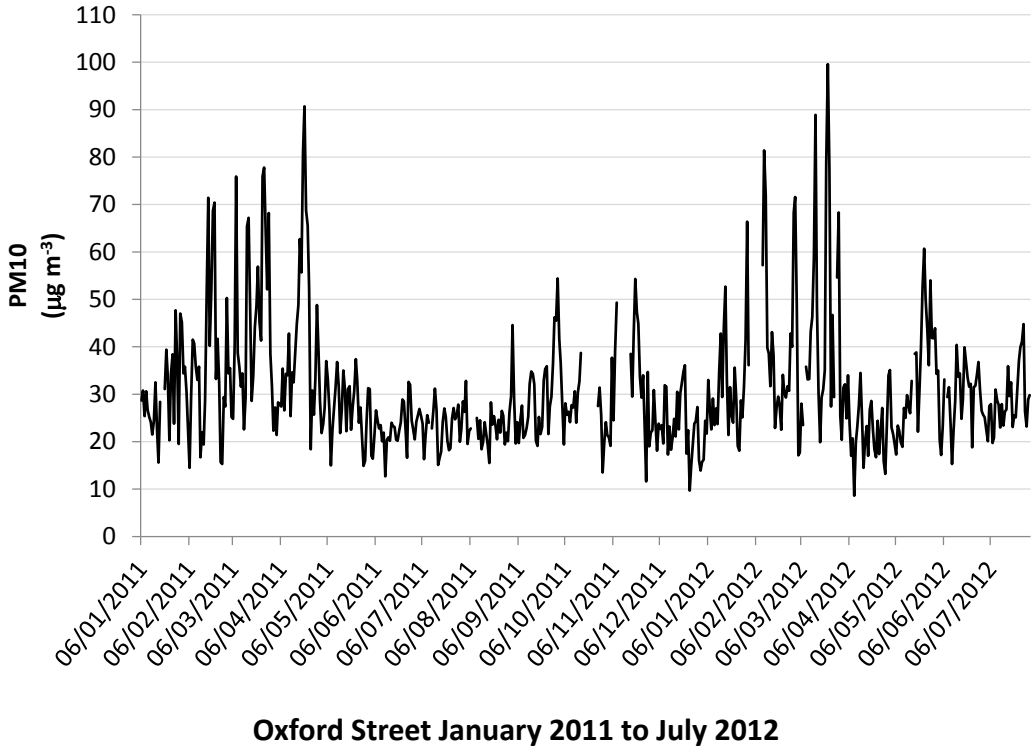

*Figure 3.10* *PM10 mass concentrations measured at Marylebone Road, 2002 – 2012 (n = 2914) (Partisol 2025 sampler)*



### OXFORD STREET JANUARY 2011 – JULY 2012

Monitoring at this site was carried out by King's College London (KCL) on behalf of Westminster City Council and data are available from the Londonair website (www.londonair.org.uk). Figure 3.11 is the time series plot of this dataset. The samples were collected gravimetrically with a Partisol 2025 sampler and the filter substrate for the entire period was Emfab™. The data used in this project cover the period 1 January 2011 to 31 July 2012.

*Figure 3.11* *PM10 mass concentrations measured at Oxford Street, 2011 – July 2012 (n = 553) (Partisol 2025 sampler)*



## ALL SITES

Table 3.4 sets out details of the mass concentrations measured at each site. Concentrations for North Kensington and Marylebone Road have been separated between 2002 – 2006 and 2009 – 2012. The distribution of the data at each site is illustrated by way of boxplots in Figure 3.12.

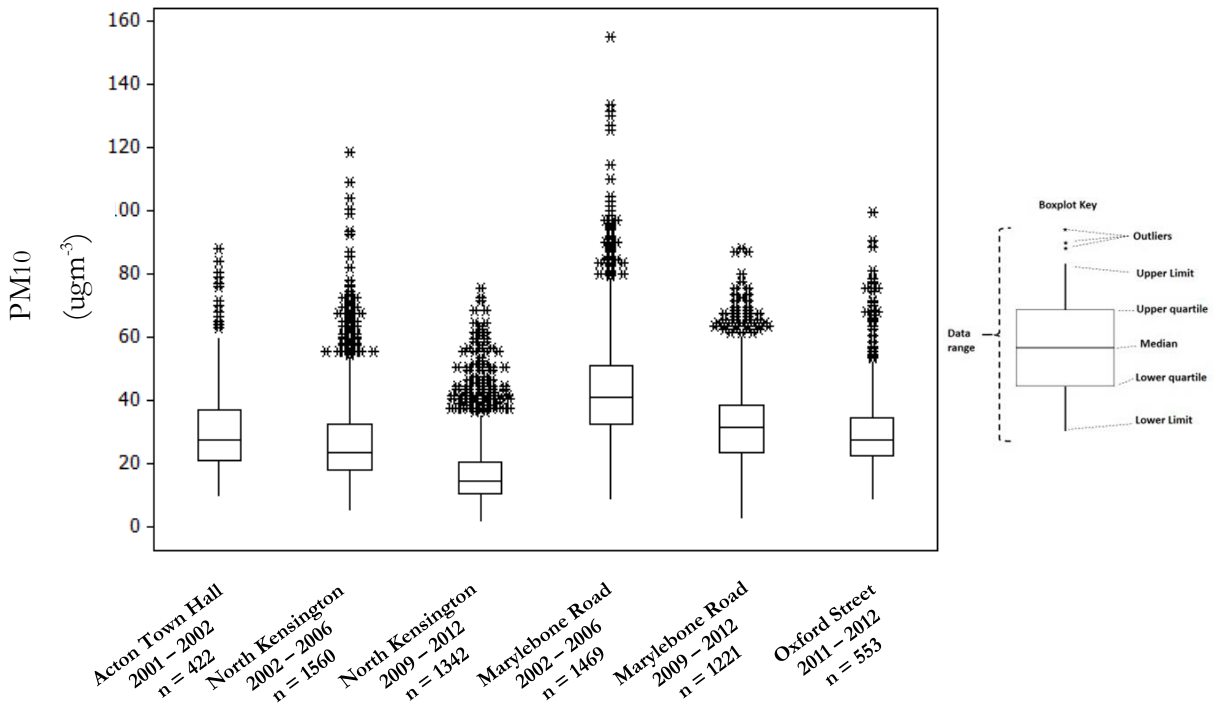
Differences between the concentrations collected on the two different filter substrates were also distinctive, with lower concentrations measured at North Kensington and Marylebone Road after the change of filter substrate in 2007. The concentrations measured at Acton Town Hall in 2001 and 2002 were very similar to those measured at Oxford Street ten years later but the filter substrates were different at the two sites. Quartz fibre was used as the filter substrate at Acton Town Hall and therefore any comparison between these two sites needs to be treated with some caution. However the Acton Town Hall concentrations may be compared with those collected at North Kensington and Marylebone Road before the filter change. Indeed PM10 mass concentrations at Acton Town Hall seem more analogous with the concentrations measured at North Kensington than those measured at Marylebone Road, perhaps reflecting the nature of Acton Town Hall as a suburban roadside site.

Distinct differences in the PM10 mass concentrations measured at North Kensington and Marylebone Road were observable when comparing the same time periods and filter substrate with mean mass concentrations measured at North Kensington being at least 40% lower. However, mean mass concentrations measured at Oxford Street are very similar to those measured at a similar time period at Marylebone Road although Oxford Street recorded a higher maximum mass concentration than Marylebone Road. The mass concentration at Marylebone Road on 23 March 2012 (i.e. the date when maximum concentrations were recorded at North Kensington and Oxford Street) was 80.0 μg $m^{-3}$ so was also a high pollution day when the Daily Limit Value was substantially breached.

*Table 3.4 Details of PM10 concentrations at the sampling locations 2001 - 2012*

| Site | Sampling period | No of sample days | Arithmetic mean (95% C.I.s) | Maximum (date) |
|---|---|---|---|---|
| | **PM10 (µg $m^{-3}$)** | | | |
| | **Quartz fibre** | | | |
| Acton Town Hall | January 2001 – December 2002 | 422 | 30.9 (29.6,32.2) | 88.3 (3.11.01) |
| North Kensington | 2002 – 2006 | 1560 | 27.7 (27.0,28.4) | 118.6 (29.3.03) |
| Marylebone Road | 2002 - 2006 | 1469 | 44.2 (43.3,45.1) | 155.0 (23.11.06) |
| | **Emfab™** | | | |
| North Kensington | 2009 - 2012 | 1342 | 18.1 (17.5,18.6) | 76.0 (23.3.12) |
| Marylebone Road | 2009 - 2012 | 1221 | 32.7 (32,33.4) | 88.0 (10.1.09) |
| Oxford Street | 2011 - 2012 | 553 | 31.1 (30.0,32.2) | 99.6 (23.3.12) |

*Figure 3.12 Boxplots illustrating the distribution of mass concentrations of PM10 measured at all the study locations 2001 - 2012*



## *Trend Analysis ($PM_{10}$ concentrations)*

Trend analysis was carried out using the TheilSen function within the Openair software package (Carslaw and Ropkins, 2012) using the R language as set out in chapter 2. Figures 3.13 to 3.18 are the results of this analysis at each of the sampling sites. How to interpret these charts and their associated uncertainty are set out in chapter 2. Details of each trend are set out in Table 3.5.

It is clear that between 2002 and 2006 both North Kensington and Marylebone Road experienced a significant upward trend in concentrations which is in line with trends reported by Fuller and Green (2006) and Harrison et al. (2008) for the same, or parts of the same, period. The trend at Acton Town Hall is upward but it should be noted that there are a number of gaps in the data and the dataset is small to consider trends. Despite the short timescale, it is important to note that the trend at Acton Town Hall is nevertheless similar to those reported at the other locations at the same time.

The trends at North Kensington, Marylebone Road and Oxford Street (Figures 3.15, 3.17 and 3.18) during 2009 – 2012 are, however, different and at each site a small downward trend is reported. However, none of these trends are significant at $p < 0.1$ and it is perhaps more appropriate to consider that there has been no real trend in $PM_{10}$ concentrations at any of these sites during 2009 to 2012.

*Table 3. 5* *Summary of TheilSen analysis of trends and statistical significance, PM10 all sites 2001 – 2012*

| Site | Sampling period | No of sample days | Trend (µg $m^{-3}$) per year (95% C.I.s) | p |
|---|---|---|---|---|
| Acton Town Hall | 2001 – 2002 | 422 | 1.92 (-1.65,5.62) | >0.1 |
| | | | | |
| North Kensington | 2002 - 2006 | 1560 | 1.43 (0.69,2.29) | <0.001 |
| Marylebone Road | 2002 - 2006 | 1469 | 0.90 (-0.28,1.98) | <0.1 |
| | | | | |
| North Kensington | 2009 - 2012 | 1342 | -0.63 (-1.92,0.85) | >0.1 |
| Marylebone Road | 2009 - 2012 | 1221 | -0.39 (-1.46,0.6) | >0.1 |
| | | | | |
| Oxford Street | 2011 - 2012 | 553 | -0.76 (-9.9,6.92) | >0.1 |

*Figure 3.13* *TheilSen trend analysis, PM10, Acton Town Hall, 2001 – 2002 (p >0.1)*

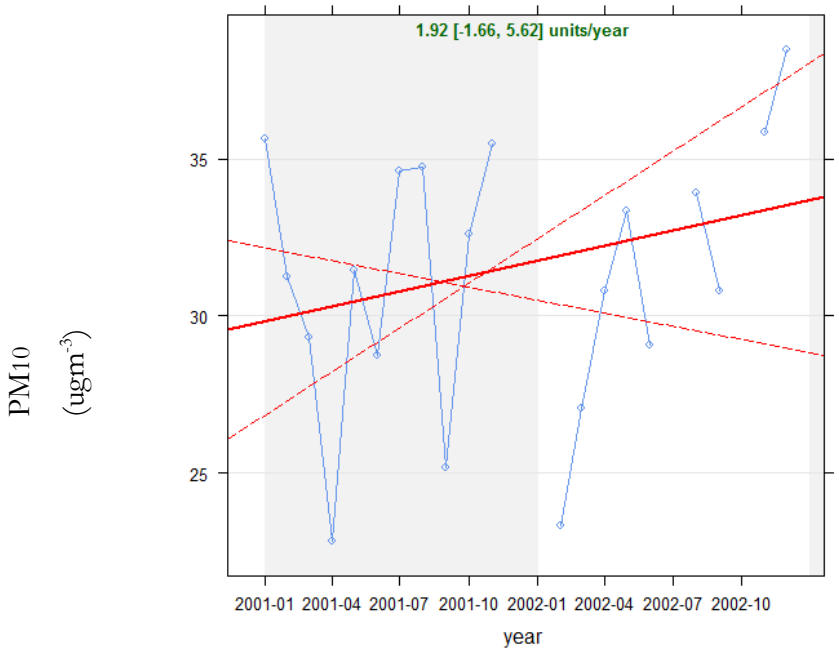


*Figure 3.14* *TheilSen trend analysis, PM10 North Kensington, 2002 – 2006 (quartz fibre filters)* ***(p = <0.001)***

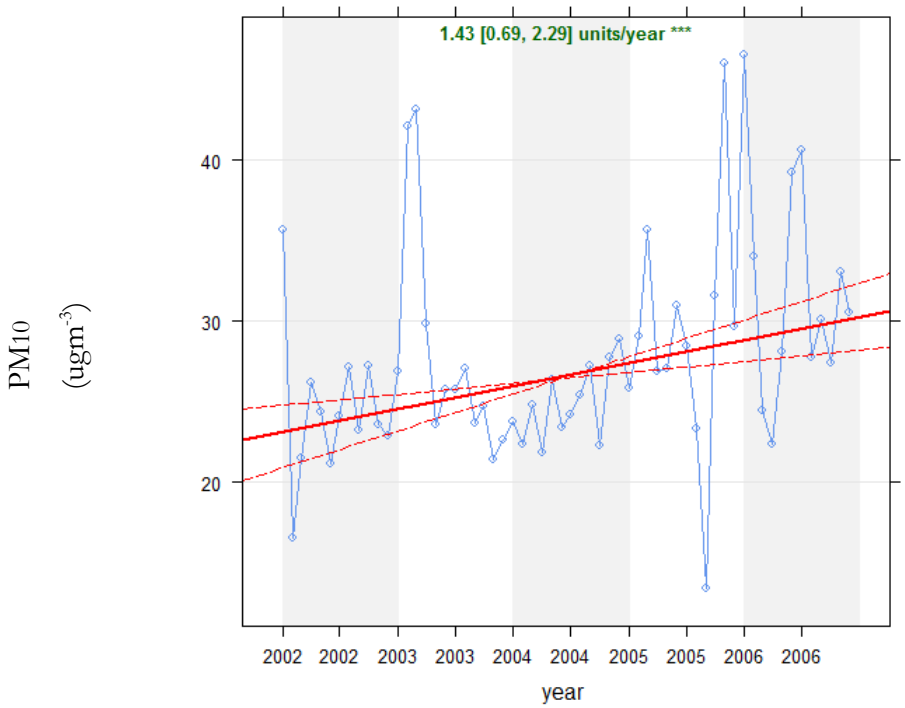



*Figure 3.15* *TheilSen trend analysis, PM10 North Kensington, 2009 – 2012 (Emfab™)* ***(p = <0.001)***

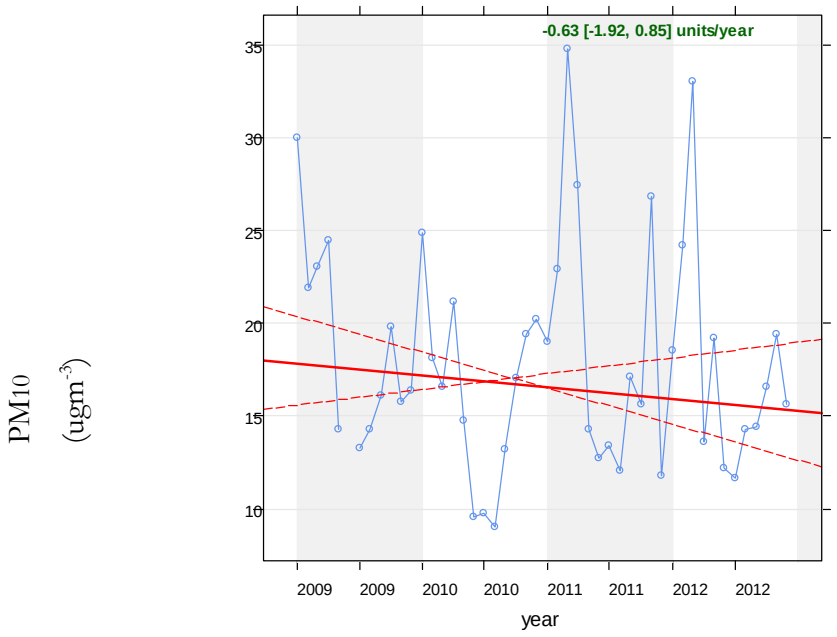


*Figure 3.16* *TheilSen trend analysis, PM10 Marylebone Road, 2002 – 2006 (quartz fibre filters)*

***(p = <0.1)***

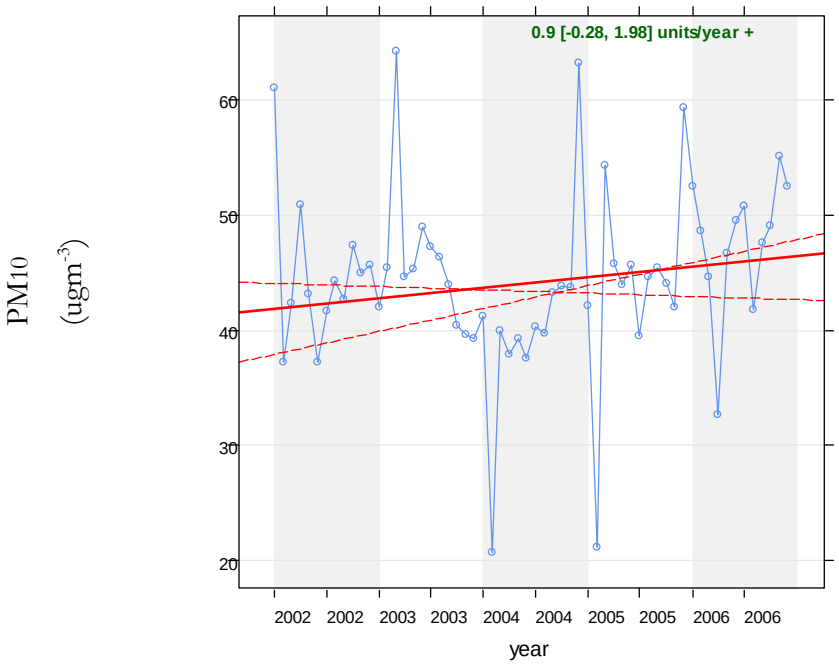



*Figure 3.17* *TheilSen trend analysis, PM10 Marylebone Road, 2009 – 2012 (Emfab™)*

***(p = >0.1)***

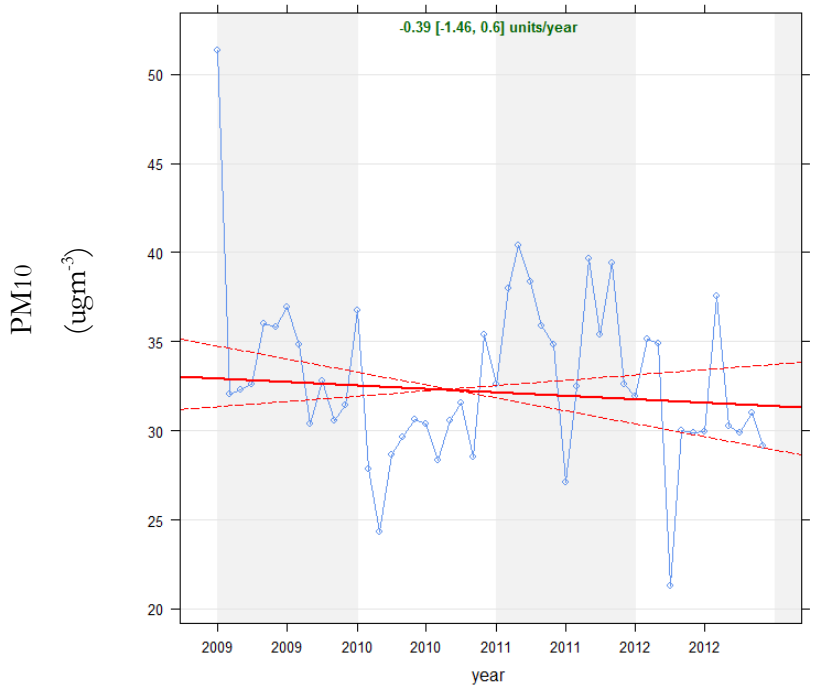
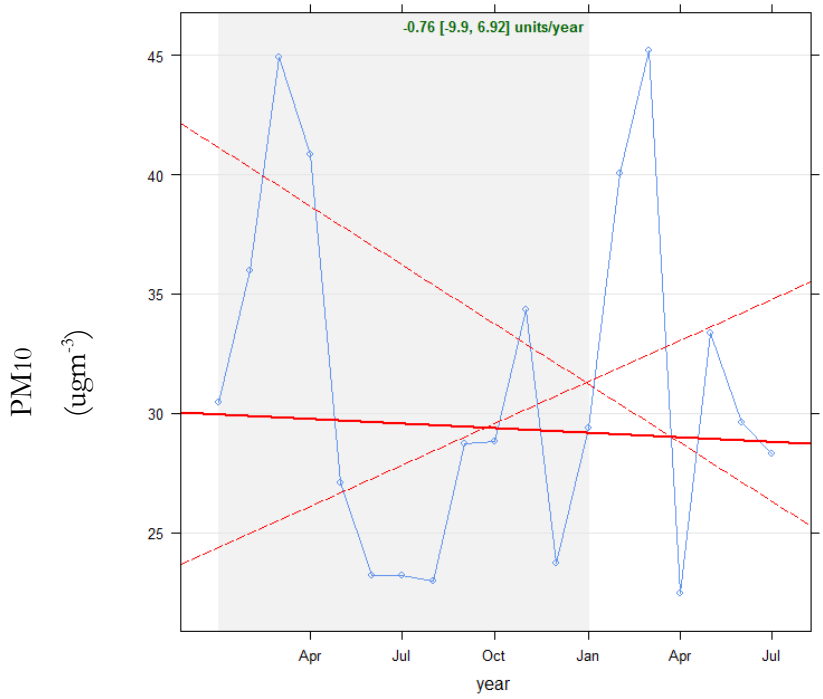


*Figure 3.18* *TheilSen trend analysis, PM10 Oxford Street, 2011 – 2012 (Emfab™)*

**(p = >0.1)**



## *Day of the week and Monthly Trends*

The timeVariation function within the Openair software package (Carslaw and Ropkins, 2012) has been utilised to consider both day of the week and monthly trends.

Day of the week trends of PM10 at each sampling site are illustrated in Figures 3.19 to 3.22. At each site mean concentrations were lowest on Sundays indicating that human activity is an important influence on PM concentrations. Weekday/weekend differences were also noted by AQEG (2005) at Marylebone Road in 2002 – 2003. At the trafficked sites (Marylebone Road, Oxford Street and Acton Town Hall) the difference between Sunday and weekday means was in the region of 20% but it is slightly less at North Kensington where the reduction (across the whole sampling period) was in the region of 15%. It is possible that weekday/weekend variation was determined by local primary particle sources that made a proportionately greater contribution to concentrations at Marylebone Road when compared with North Kensington.

Concentrations also appeared to be slightly lower on Mondays than on other days of the working week (Monday to Friday). Jenkin et al. (2002) noted a similar day of week variation in ozone concentrations in the UK and suggested that it may be due to a temporal dependence in the emissions of precursor species and therefore lower concentrations on Mondays may be due to lower weekend concentrations of precursor species elsewhere.

The shading in the following figures indicates the uncertainty associated with the measurements as represented by the 95% confidence intervals. As may be seen there was considerable overlap in the 95% CIs in the earlier, pre 2005, datasets but there was a clearer reduction in PM concentrations on Sundays after 2009.

*Figure 3.19 Day of the week variation in PM10 concentrations at Acton Town Hall, 2001 - 2002*

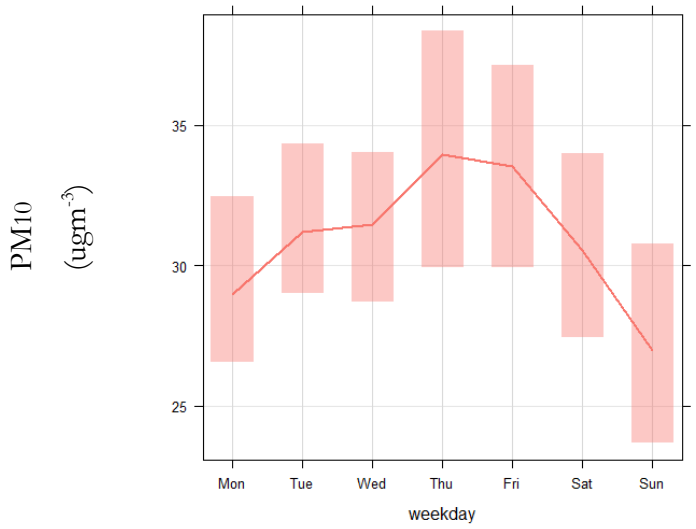
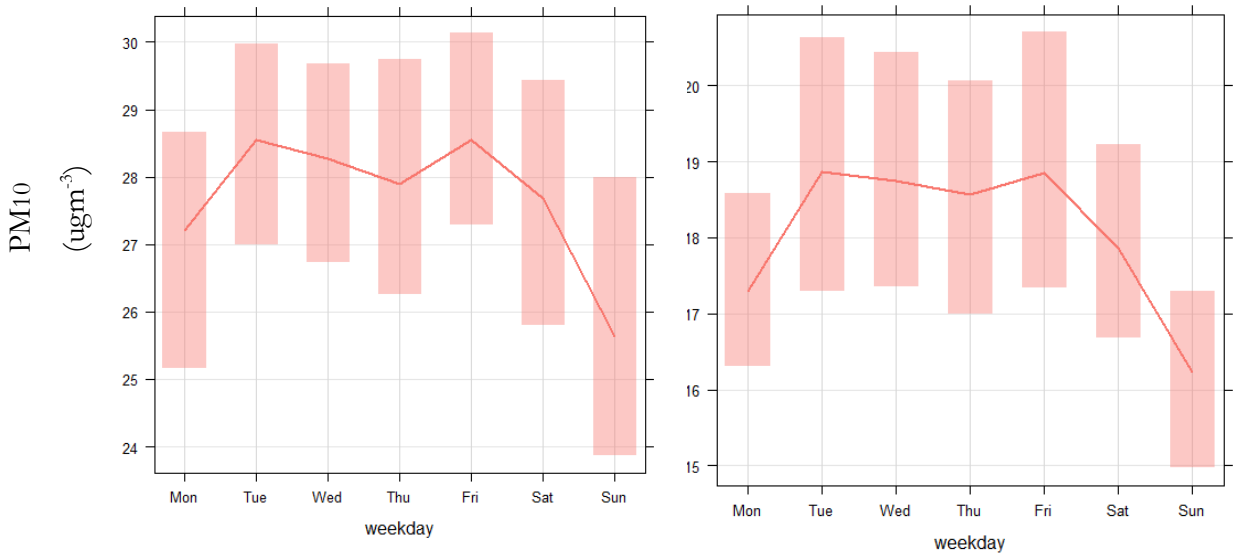



*Figure 3.20 (a) and (b) Day of the week variation in PM10 concentrations at North Kensington (a) 2002 – 2006 and (b) 2009 - 2012*

(a) (b)




**NB Different y axes**

*Figure 3.21(a) and (b)* *Day of the week variation in PM10 concentrations at Marylebone Road (a) 2002 – 2006 and (b) 2009 – 2012*

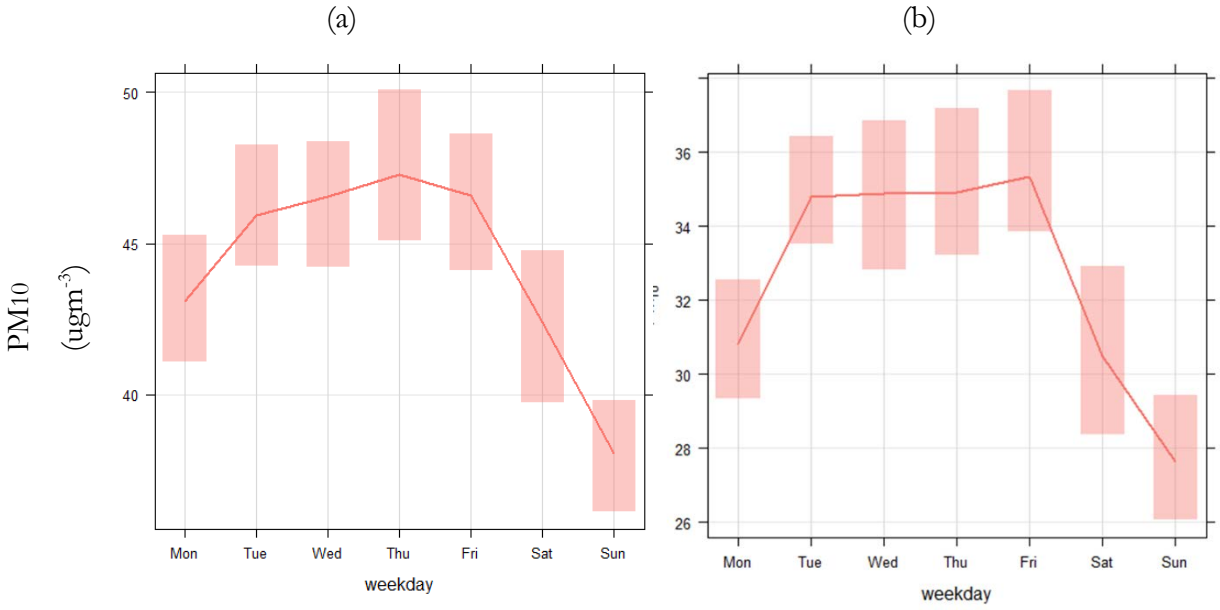
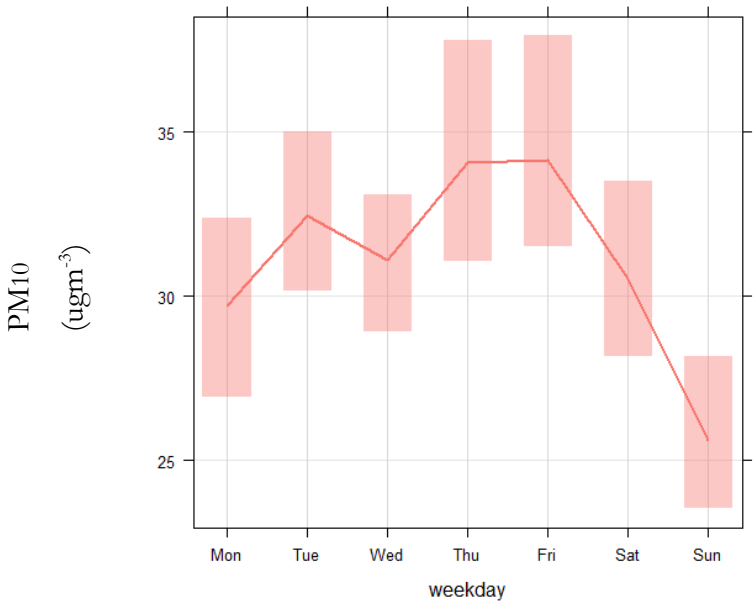



*Figure 3.22* *Day of the week variation in PM10 concentrations at Oxford Street, 2011 - 2012*




**NB Different y axes**

Monthly trends are set out in figures 3. 23 to 3.26. It is clear by simply looking at these figures that, at each of the sites other than Acton Town Hall concentrations seem to be at their greatest in March of each year. The results for Acton Town Hall may not be typical as data availability is lower than at the other sites and there is considerable overlap between the standard deviation reported for each month. It is worth considering first whether there has been any change over time at North Kensington and Marylebone Road which have the longer term datasets. Whilst concentrations will be different in the two reported periods (2002/2006 and 2009/2012) because of the change of filter substrate previously discussed, this should not have any influence on monthly variation. Nevertheless there are differences between the two time periods at both sites. At North Kensington between 2002 and 2006 concentrations were lower during the summer and autumn months but during 2009 and 2012 there was a more marked rise in concentrations in the autumn months (September, October, November). At Marylebone Road the opposite trend seems to be the case with lowest concentrations occurring during the summer months in 2002 – 2006 with a rise in concentrations in the autumn months. Concentrations in the autumn months seem to be lower at Marylebone Road between 2009 and 2012.

The trends at Oxford Street, whilst included here for completeness, need to be treated with more caution as the dataset only spans 19 months (January 2011 to July 2012). Therefore two months are included between January and July but only one month's data for each of August to December.

A peak in PM concentrations in the spring months has been noted elsewhere (see, for example, Smith et al., 2001, Harrison and Yin, 2008 and Harrison et al., 2012). It is considered to be due to a number of different factors occurring mainly in the fine fraction, including meteorological influences, reduced dispersion, increased availability of ammonia (from land management practices), loss of semi-volatile species in the summer months Some of these factors are further explored in chapter 4.

In summary day of week variation is very similar at each site but monthly variation shows different behaviour not only from site to site but also from year to year.

*Figure 3.23 Monthly variation in PM10 concentrations at Acton Town Hall, 2001 - 2002*

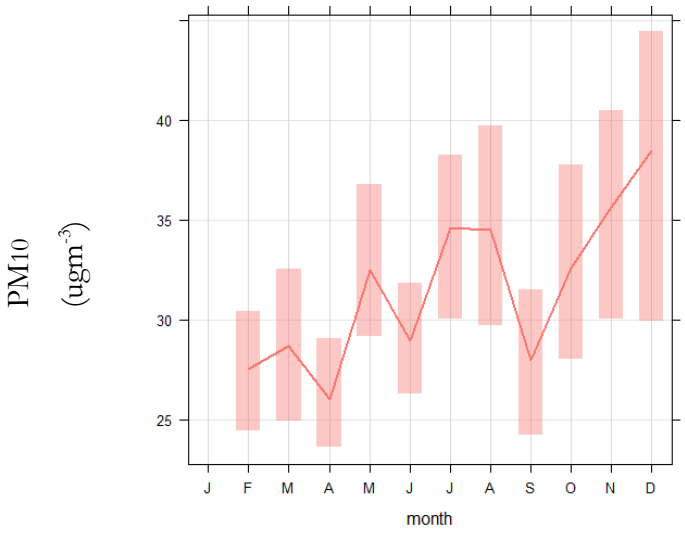
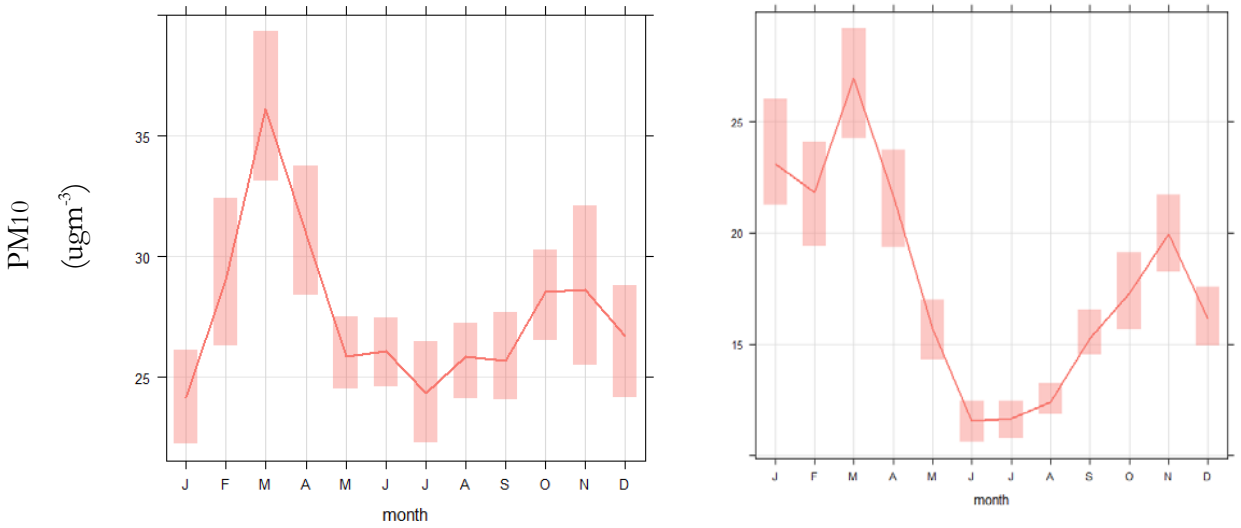



*Figure 3.24 (a) and (b) Monthly variation in PM10 concentrations at North Kensington (a) 2002 – 2006 and (b) 2009 – 2012*

**(a)** **(b)**




**NB Different y axes**

*Figure 3.25 (a) and (b) Monthly variation in PM10 concentrations at Marylebone Road (a) 2002 – 2006 and (b) 2009 – 2012*

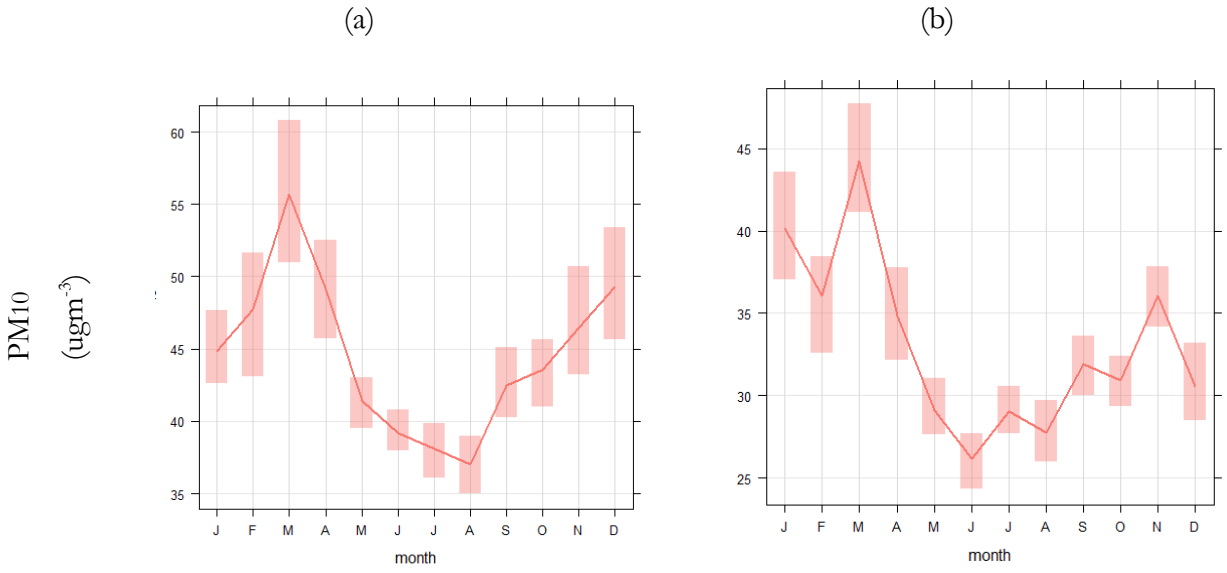
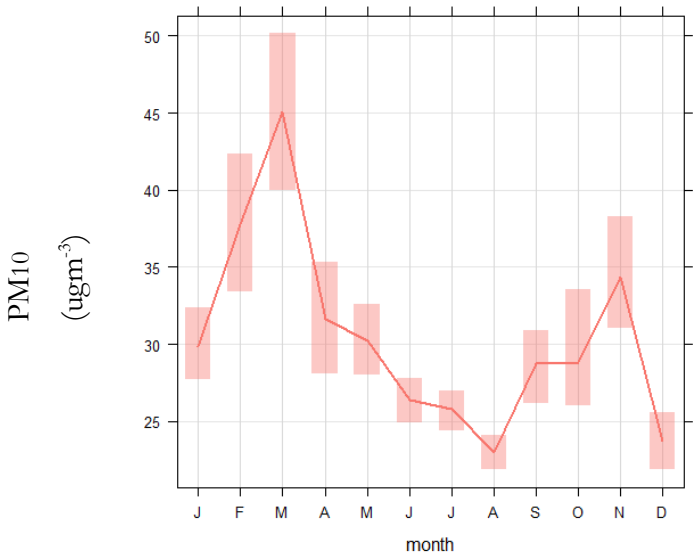



*Figure 3.26 Monthly variation in PM10 concentrations at Oxford Street, 2011 - 2012*




**NB Different y axes**

As may be seen from the time series data presented above, PM10 concentrations vary on a daily basis and there are excursions above the Daily Limit Value at all of the sites. It is also notable that there is no baseline concentration from which elevated episodes stand out. Build-up of concentrations may happen quickly and similarly disperse rapidly but at different rates at different times.

In order to understand the variation in PM10 mass both at and between locations, the mass concentration data have been grouped into 10 μg $m^{-3}$ 'bins'. The number of sample days in each concentration 'bin' is illustrated in Figure 3.27. There is a great deal of variation in the number of days in each dataset and, in order to compare differences between the different locations, it is perhaps more informative to consider the percentage number of days in each concentration 'bin' - see Figure 3. 28.

Table 3.6 summarises the data illustrated in Figures 3.27 and 3.28. At Acton Town Hall, North Kensington and Oxford Street the majority of days fell below a daily concentration of 30 μg $m^{-3}$. Although at both Acton Town Hall and Oxford Street a further quarter of all sample days were within the 30 – 40 μg $m^{-3}$ concentration 'bin'. A different pattern emerges at Marylebone Road. Between 2002 and 2006 only 18% of sample days were below 30 μg $m^{-3}$ in contrast to 68% at North Kensington and 29% of days at Marylebone Road were above 50 μg $m^{-3}$ (i.e. in the region of 3 times the permitted number of days when the Daily Limit Value could be exceeded) compared to 7% at North Kensington. The change of filter substrate in 2007 undoubtedly influenced this distribution. 88% of sample days were below 30 μg $m^{-3}$ at North Kensington between 2009 and 2012 and 43% at Marylebone Road. The number of days when the Daily Limit Value was exceeded reduced at Marylebone Road from 29% between 2002 and 2006 as reported above to 9% during the period 2009 – 2012.

Days when the Daily Limit Value was exceeded at each site have been looked at in more detail on a year by year basis in the next section.

*Table 3.6 Number of sample days (and percentage to overall sample number) grouped by 10 µg $m^{-3}$ increments in PM concentration at each sampling location 2001 - 2012*

| Site | **PM 10 concentration 'bin' (µg $m^{-3}$)** | | | | | |
|---|---|---|---|---|---|---|
| | **<20** | **20 - 30** | **30-40** | **40 - 50** | **50- 60** | **>60** |
| | No of sample days (%age of total sample days) | | | | | |
| | **Quartz filters** | | | | | |
| Acton Town Hall 2001 -2002 | 84 (20%) | 159 (38%) | 95 (23%) | 37 (9%) | 31 (7%) | 16 (4%) |
| North Kensington 2002 – 2006 | 483 (31%) | 583 (37%) | 256 (16%) | 123 (8%) | 51 (3%) | 64 (4%) |
| Marylebone Road 2002 - 2006 | 38 (3%) | 226 (15%) | 411 (28%) | 373 (25%) | 207 (14%) | 214 (15%) |
| | **Emfab™ filters** | | | | | |
| North Kensington 2009 - 2012 | 942 (70%) | 242 (18%) | 83 (6%) | 38 (3%) | 23 (2%) | 14 (1%) |
| Marylebone Road 2009 - 2012 | 186 (15%) | 337 (28%) | 411 (34%) | 168 (14%) | 67 (5%) | 52 (4%) |
| Oxford Street 2011 - 2012 | 72 (13%) | 249 (45%) | 138 (25%) | 50 (9%) | 17 (3%) | 27 (5%) |

*Figure 3.27 Comparison of number of days in each PM10 concentration 'bin' between sampling locations*

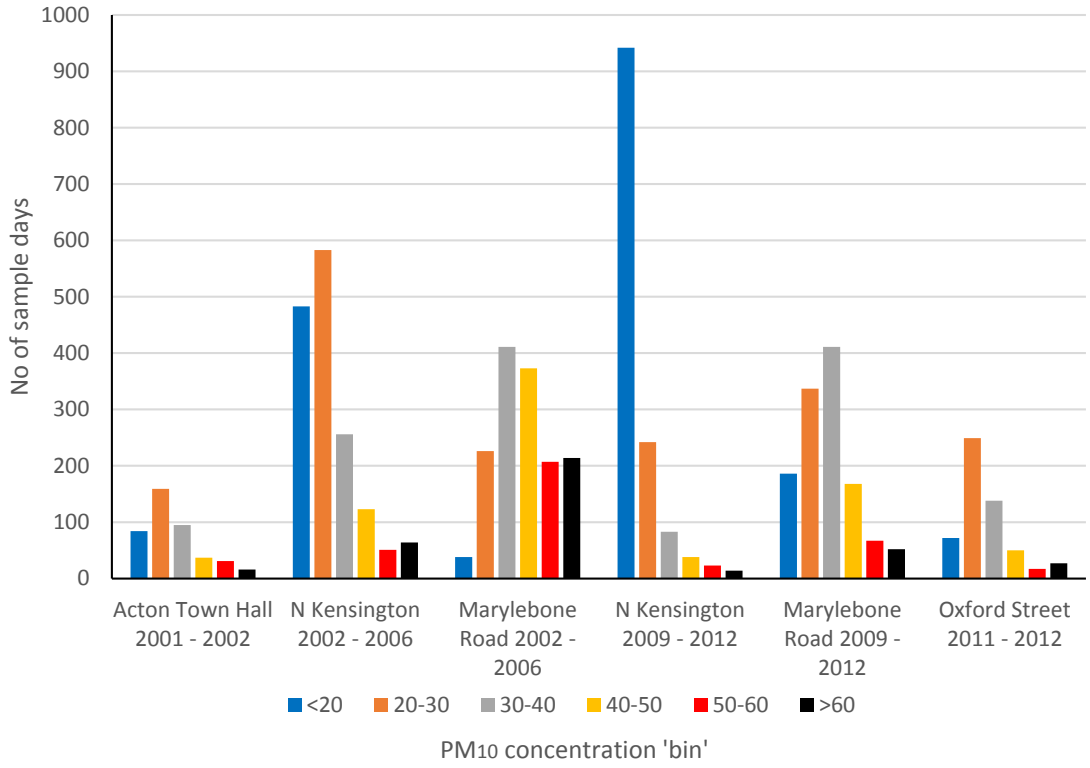
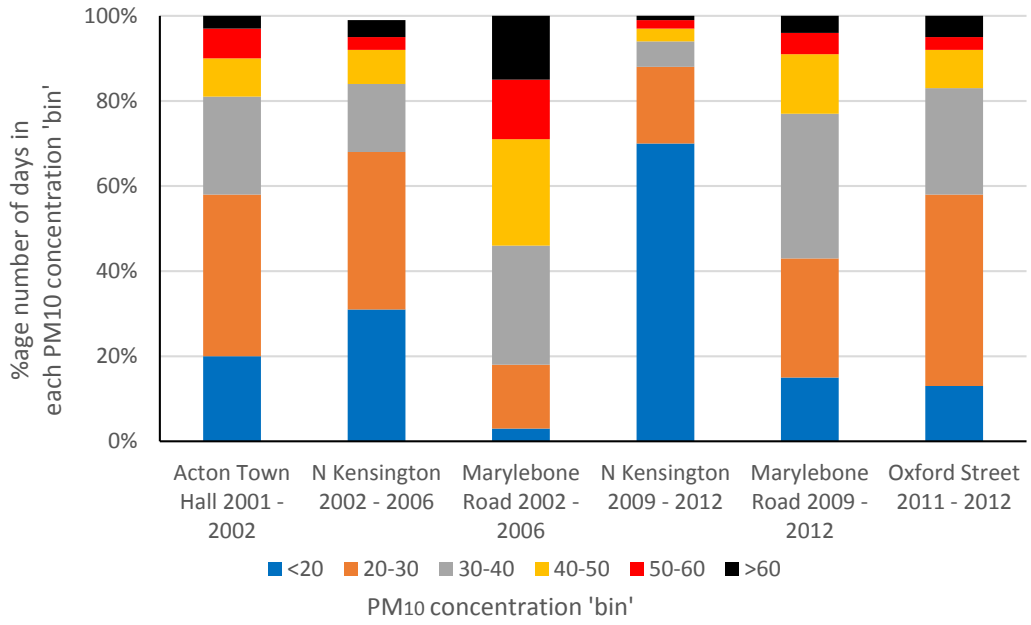



*Figure 3.28 Comparison of percentage number of days in each PM10 concentration 'bin' between sampling locations*



## *High pollution days*

As set out in chapter 1, regulatory standards for PM10 require that both annual mean concentrations (40 μg $m^{-3}$) and Daily Limit Values (50 μg $m^{-3}$ - not be exceeded on more than 35 days per year) be met.

The number of days when the Daily Limit Value has been exceeded at each site in each calendar year are set out in Table 3.7. Setting aside the data capture requirements in the EU Directive, if the Daily Limit Value of no more than 35 days on which concentrations may exceed 50 μg $m^{-3}$ each year is translated (very roughly) to no more than approximately 10% of sample days then it may be seen that at most sites up to 2006 this limit was exceeded most years. There were fewer excursions at North Kensington in this period, notably in 2002 and 2004. During the period 2009 to 2012 there were fewer days when the daily limit value ('DLV') was exceeded. It is however difficult to be certain whether the number of recorded high pollution days before 2006 was influenced by the filter substrate and its associated artefacts or whether real improvements in ambient air quality have been achieved since 2009. There would seem to have been a reduction in the number of days when the DLV was exceeded in 2010 but this was not repeated in 2011 and 2012. Indeed at the Oxford Street site there was an increase in the percentage number of days when the DLV was exceeded in 2012, bearing in mind that there were only 7 months of that year in the dataset.

*Table 3.7* *Number of days when PM10 mass concentrations exceeded 50 μg $m^{-3}$ at each sampling location, 2001 - 2012*

| **Number of days above 50 μg $m^{-3}$ at each site (% sample days)** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **2001** | **2002** | **2003** | **2004** | **2005** | **2006** | **2009** | **2010** | **2011** | **2012** |
| **Acton Town Hall** | 26 (11%) | 22 (12%) | - | - | - | - | - | - | - | - |
| **North Kensington** | - | 14 (4%) | 34 11%) | 12 (4%) | 25 (9%) | 30 (9%) | 9 (3%) | 2 (0.6%) | 14 (4%) | 12 (3%) |
| **Marylebone Road** | - | 66 (27%) | 96 (30%) | 68 (22%) | 85 (26%) | 106 (38%) | 37 (13%) | 16 (5%) | 36 13%) | 30 (9%) |
| **Oxford Street** | - | - | - | - | - | - | - | - | 25 (7%) | 19 (9%) |
| **Filter substrate** | **QUARTZ** | | | | | | **EMFAB™** | | | |

# $PM_{2.5}$ mass concentrations

In order to understand the variation in the PM10 concentrations reported above both at and between the locations, it is important to try and understand, as far as possible, what is happening in the various sources which contribute to that variation. At three of the sampling locations measurements of the fine PM fraction, PM2.5, were also available. No PM2.5 measurements were made at Oxford Street. The opportunity has therefore been taken to ascertain the contribution made to overall PM10 concentrations by this size fraction and whether it is more or less influential on overall PM10 concentrations both at each site and during the study period.

## ACTON TOWN HALL 2001 – 2002 ($PM_{2.5}$)

Details of the PM2.5 sampling programme is described above. As mentioned, the amount of PM collected on the 'fine' filter on a dichotomous Partisol sampler has to be corrected to allow for some of this fraction collected on the 'coarse' filter. PM2.5 discussed in this section is reported with this correction.

## NORTH KENSINGTON AND MARYLEBONE ROAD 2002 – 2012 ($PM_{2.5}$)

The PM2.5 data for North Kensington and Marylebone Road were obtained from the UK Automatic Urban and Rural Network and are publicly available via both Defra's website (uk-air.defra.gov.uk) and the London Air Quality Network website (www.londonair.org.uk). In contrast to the PM2.5 data collected at Acton Town Hall these measurements were made using separate Partisol 2025 samplers co-located with the PM10 samplers. There was the same filter substrate change in 2007 (i.e. from quartz fibre to Emfab$^{TM}$) and therefore those datasets have also been sub-divided into two separate time periods, namely 2002 to 2006 and 2009 to 2012.

Figures 3.29 to 3.31 are the time series graphs for each sampling location and Figure 3.32 illustrates by way of boxplots the distribution at each site. Table 3.8 summarises the details of the mass concentrations of PM2.5 measured at each site.

*Figure 3.29* *PM2.5 mass concentrations measured at Acton Town Hall, 2001 – 2002 (n = 422), Partisol 2025 dichotomous sampler*

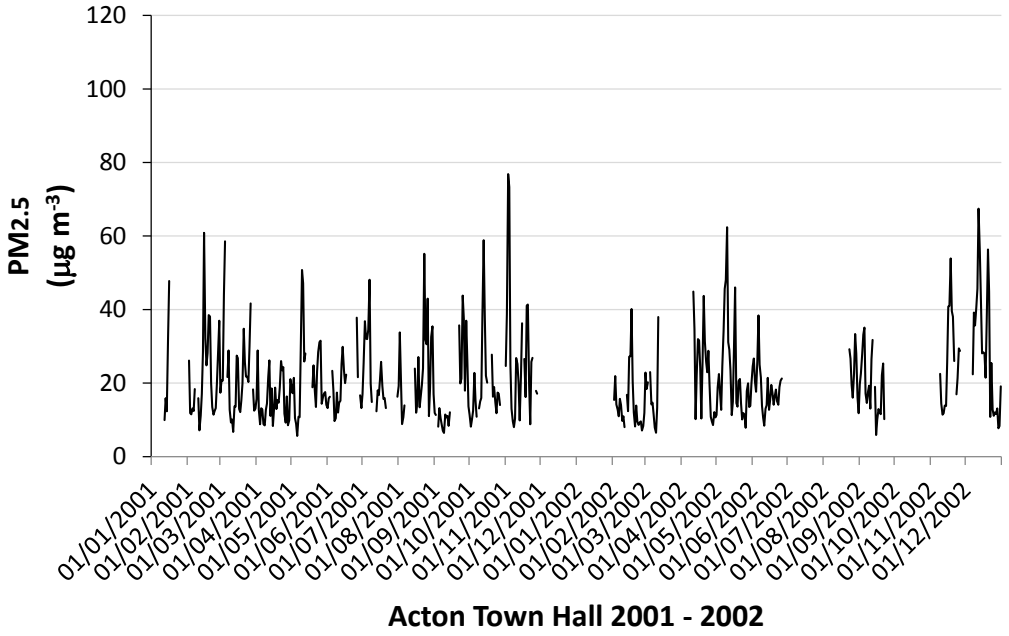



*Figure 3.30* *PM2.5 mass concentrations measured at North Kensington, 2002 – 2012 (n = 3008), Partisol 2025 sampler*

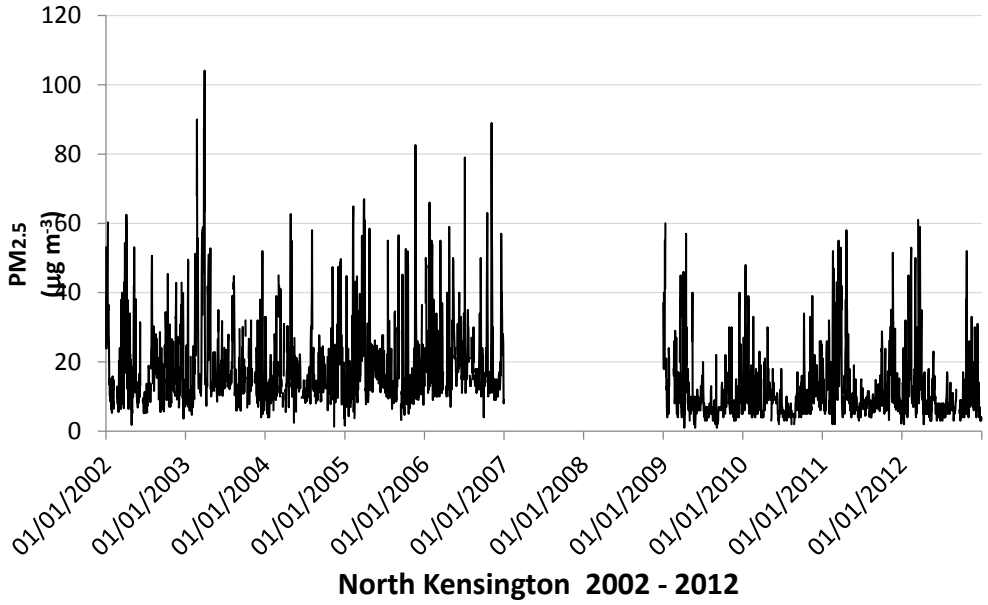


*Figure 3.31* *PM2.5 mass concentrations measured at Marylebone Road, 2002 – 2012 (n = 2066), Partisol 2025 sampler*

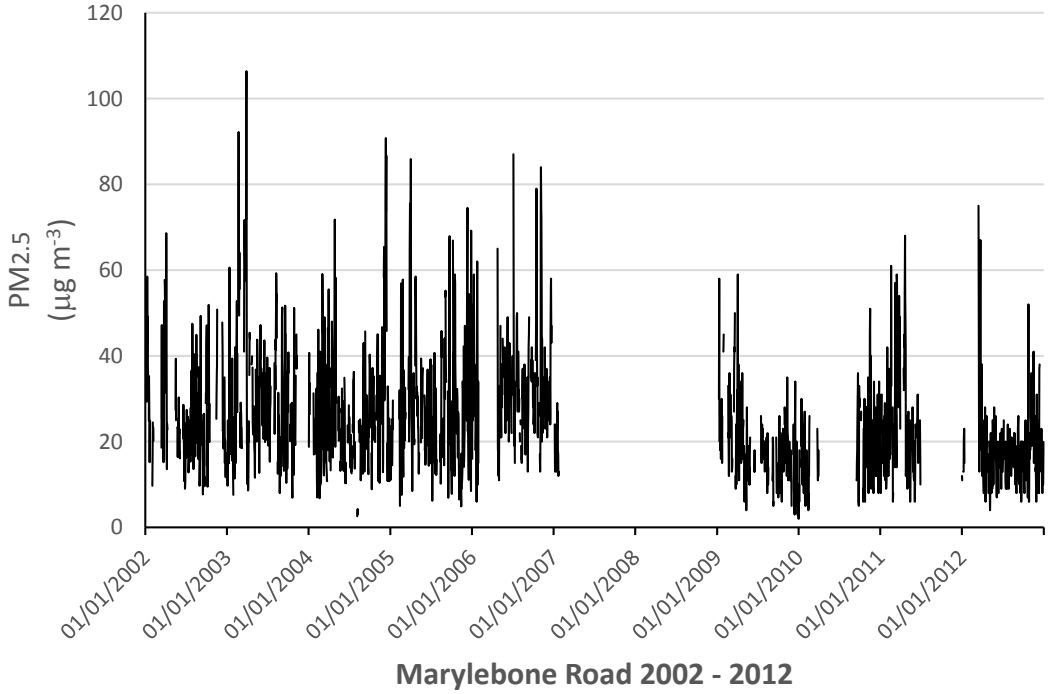



*Figure 3.32* *Boxplots illustrating the distribution of mass concentrations of PM2.5 measured at all the study locations 2001 - 2012*

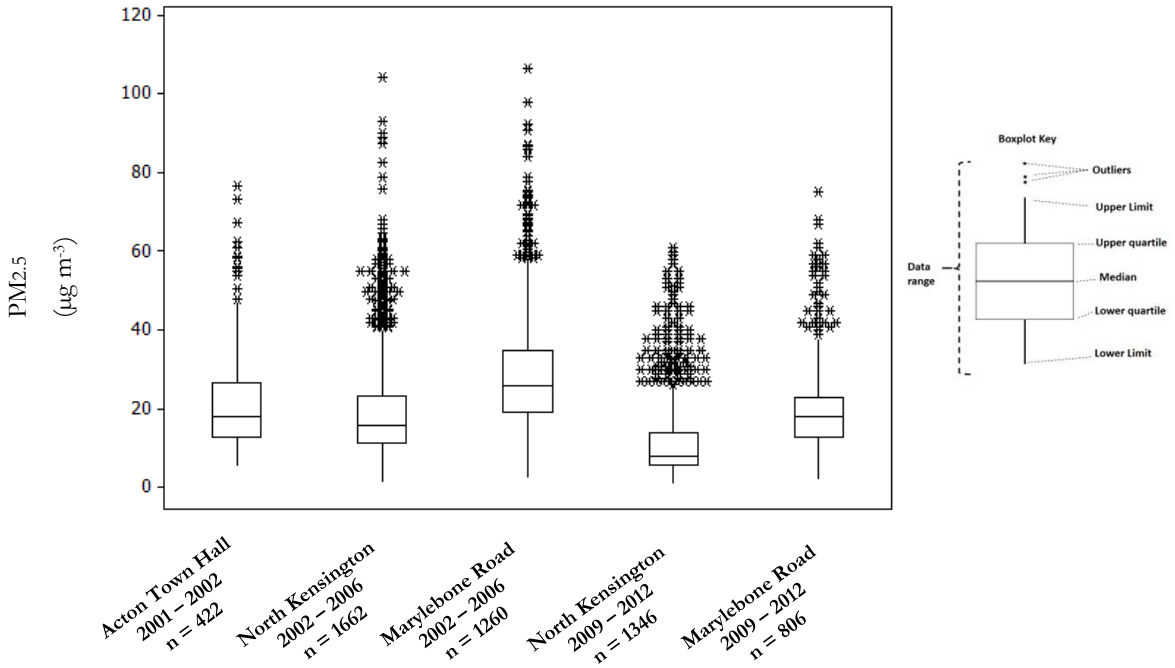


*Table 3.8 Details of PM2.5 concentrations at the sampling locations 2001 - 2012*

| Site | Sampling period | No of sample days | Arithmetic mean (95% C.I.s) | Minimum | Maximum (date) |
|---|---|---|---|---|---|
| | | | **PM2.5 (μg m-3)** | | |
| **Filter substrate** | | **Quartz fibre** | | | |
| Acton Town Hall | January 2001 – December 2002 | 422 | 21.2 (20.1,22.3) | 5.6 | 76.8 (3.11.02) |
| North Kensington | 2002 – 2006 | 1662 | 19.5 (19.0,20.1) | 1.3 | 104.1 (29.3.03) |
| Marylebone Road | 2002 - 2006 | 1260 | 28.5 (27.7,29.3) | 2.6 | 106.4 (29.3.03) |
| **Filter substrate** | | **Emfab™** | | | |
| North Kensington | 2009 - 2012 | 1346 | 11.6 (11.1,12.1) | 1.0 | 61.0 (15.3.12) |
| Marylebone Road | 2009 - 2012 | 806 | 19.3 (18.7,20.0) | 2.0 | 75.0 (15.3.12) |

Comparing the PM2.5 concentrations reported in Table 3.8 above with the PM10 concentrations reported in Table 3.4 demonstrates some changes in the contribution made by the PM2.5 fraction to overall PM10 concentrations. At Acton Town Hall (2001 – 2002) and North Kensington during 2002 to 2006 the mean contribution made by PM2.5 to mean PM10 concentrations was in the region of 70%. During 2002 to 2006 at Marylebone Road by way of contrast the contribution was in the region of 64%, i.e. approximately 6% less. At North Kensington during 2009 – 2012 the mean contribution made by PM2.5 to mean PM10 represented approximately 64% and the contribution made by PM2.5 at Marylebone Road during the same period had gone down to approximately 60%. There would therefore seem to be some evidence that the fine fraction was becoming less influential on overall PM10 concentrations and was also less influential at Marylebone Road when compared to Acton Town Hall and North Kensington. This is explored in more detail in the following sections.

## *Trend Analysis ($PM_{2.5}$ concentrations)*

Trend analysis has been carried out, using the TheilSen function in Openair (Carslaw and Ropkins, 2012), as described above, in respect of the $PM_{2.5}$ concentrations at each location, and is illustrated in Figures 3.33 to 3.37 and reported in Table 3.9 below.

When compared with the similar analysis carried out in respect of the $PM_{10}$ concentrations reported in Table 3.5 above, there are some interesting similarities. The overall trend in $PM_{2.5}$ is the same at Acton Town Hall as the $PM_{10}$ suggesting that the coarse fraction has not been changing. The trends in $PM_{2.5}$ concentrations at North Kensington and Marylebone Road were rising between 2002 and 2006 although not as steeply as the $PM_{10}$ concentrations but there appears to be very little change in the trends at each site between 2009 and 2012, similar to the $PM_{10}$ concentration trends.

*Table 3.9 Summary of TheilSen analysis of trends and statistical significance, $PM_{2.5}$ all sites 2001 – 2012*

| Site | Sampling period | No of sample days | Overall trend (μg $m^{-3}$) per year (95% C.I.s) | p |
|---|---|---|---|---|
| Acton Town Hall | 2001 – 2002 | 422 | 1.92 (-1.85, 5.56) | >0.1 |
| | | | | |
| North Kensington | 2002 - 2006 | 1662 | 0.75 (0.18,1.23) | <0.01 |
| Marylebone Road | 2002 - 2006 | 1260 | 1.09 (-0.08,1.94) | <0.05 |
| | | | | |
| North Kensington | 2009 - 2012 | 1346 | -0.27 (-1.32,0.77) | >0.1 |
| Marylebone Road | 2009 - 2012 | 806 | 0.19 (-1.87,1.54) | >0.1 |

*Figure 3.33* *TheilSen trend analysis, PM2.5, Acton Town Hall, 2001 - 2002*

**(p = >0.1)**

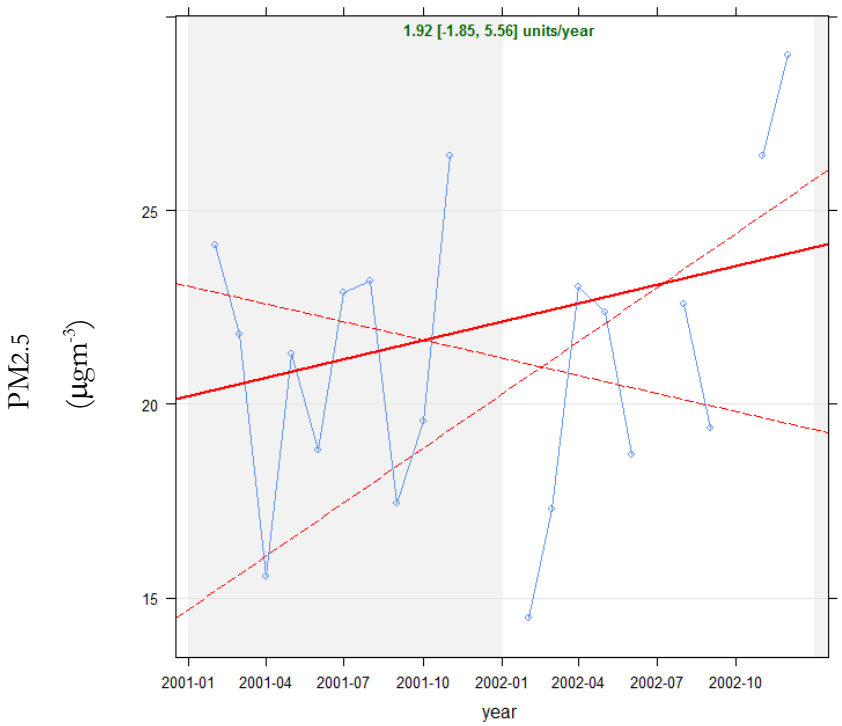


*Figure 3.34* *TheilSen trend analysis, PM2.5 North Kensington, 2002 – 2006 (quartz fibre filters)*

***(p = <0.01)***

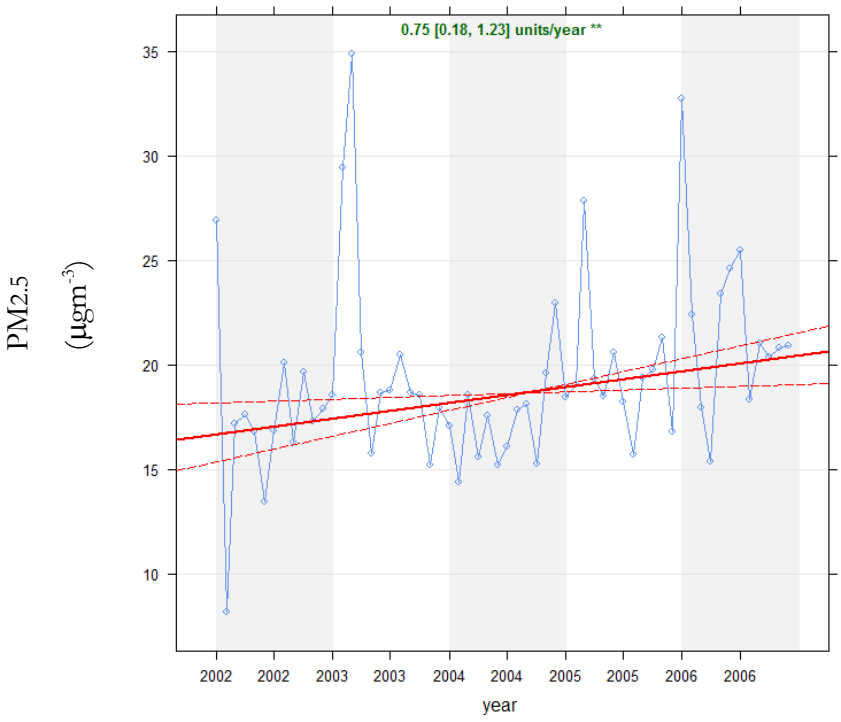



*Figure 3.35* *TheilSen trend analysis, PM2.5 North Kensington, 2009 – 2012 (Emfab™ filters)*

**(p = >0.1)**

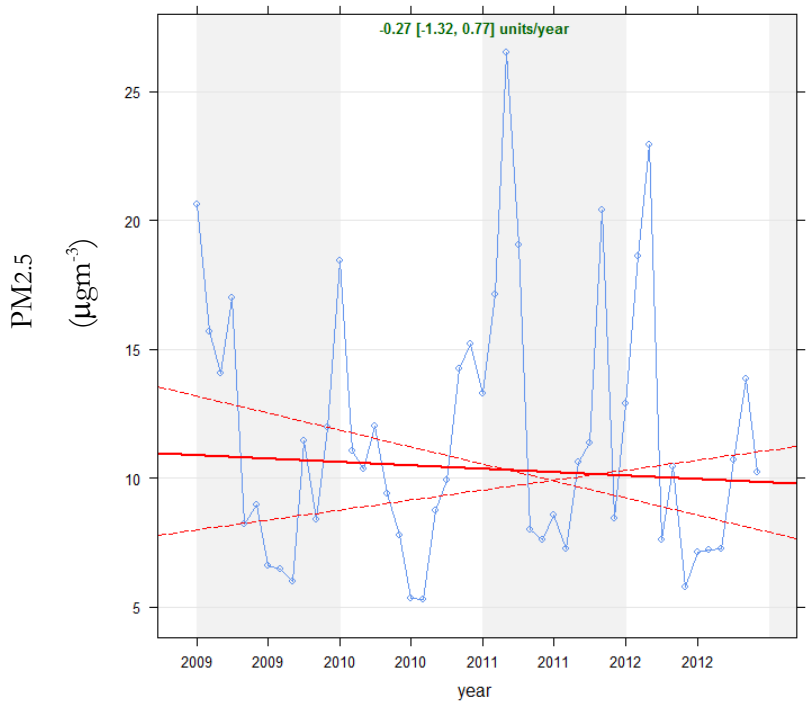


*Figure 3.36* *TheilSen trend analysis, PM2.5 Marylebone Road, 2002 – 2006 (quartz fibre filters)*

***(p = <0.05)***

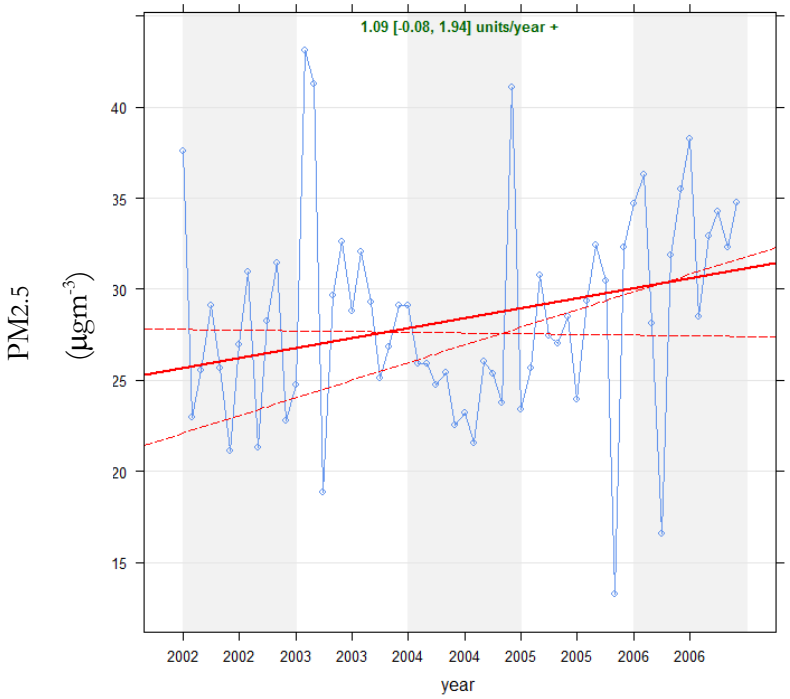
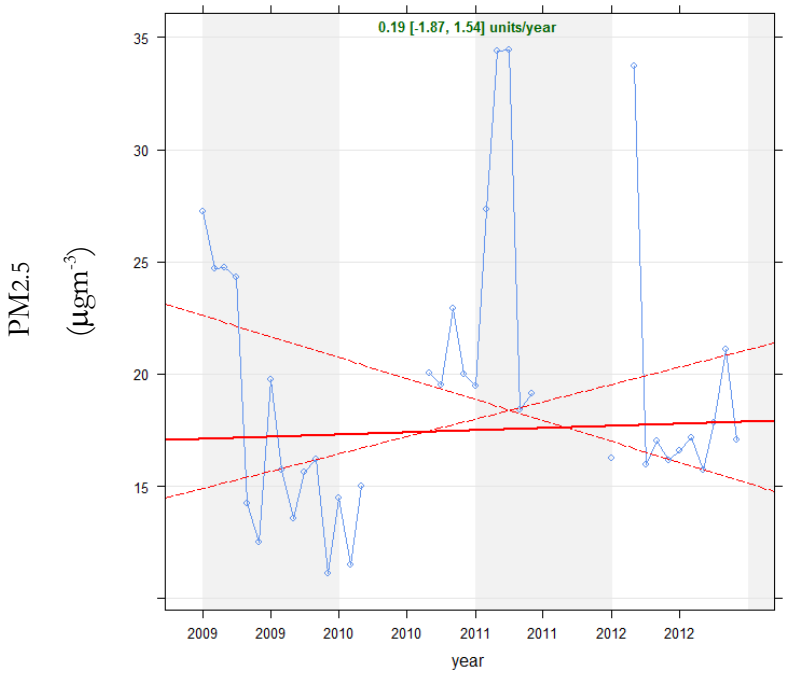



*Figure 3.37* *TheilSen trend analysis, PM2.5 Marylebone Road, 2009 – 2012 (Emfab™ filters)*

**(p = > 0.1)**



### *Day of the week and monthly trends*

The day of week trends in the $PM_{2.5}$ concentrations are very similar to those reported for the $PM_{10}$ concentrations and are not repeated in detail here. There was a similar reduction in concentrations on Sundays indicating that human activity was an important factor in $PM_{2.5}$ concentrations.

As discussed above, monthly differences are clear in the $PM_{10}$ concentrations reported above and, as discussed in chapter 1, it is suggested (see, for example, Harrison, 2012) that this is mainly as a result of an increase in secondary inorganic species which occurs in the fine fraction. Seasonal trends in $PM_{2.5}$ concentrations have therefore been considered in more detail, using the timeVariation function in Openair (Carslaw and Ropkins, 2012) again.

The results of the timeVariation analysis are set out in Figures 3.38 to 3.42.

*Figure 3.38 Monthly variation in PM2.5 concentrations at Acton Town Hall, 2001 - 2002*

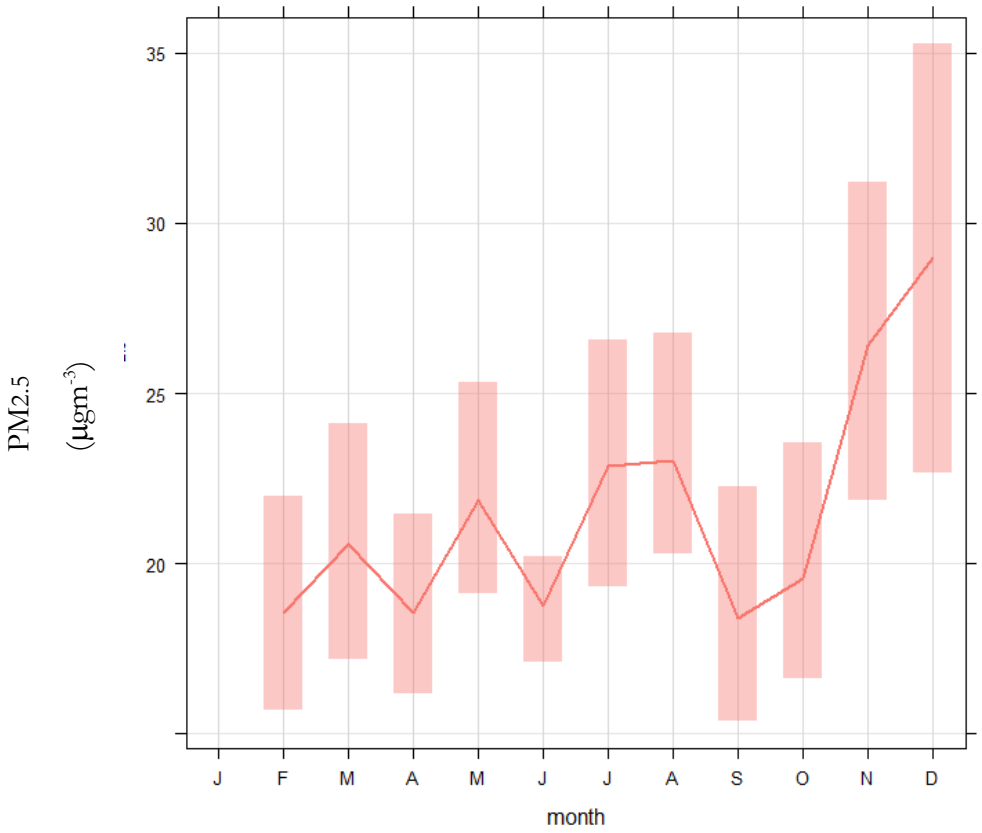


*Figure 3.39* *Monthly variation in PM2.5 concentrations at North Kensington, 2002 - 2006*

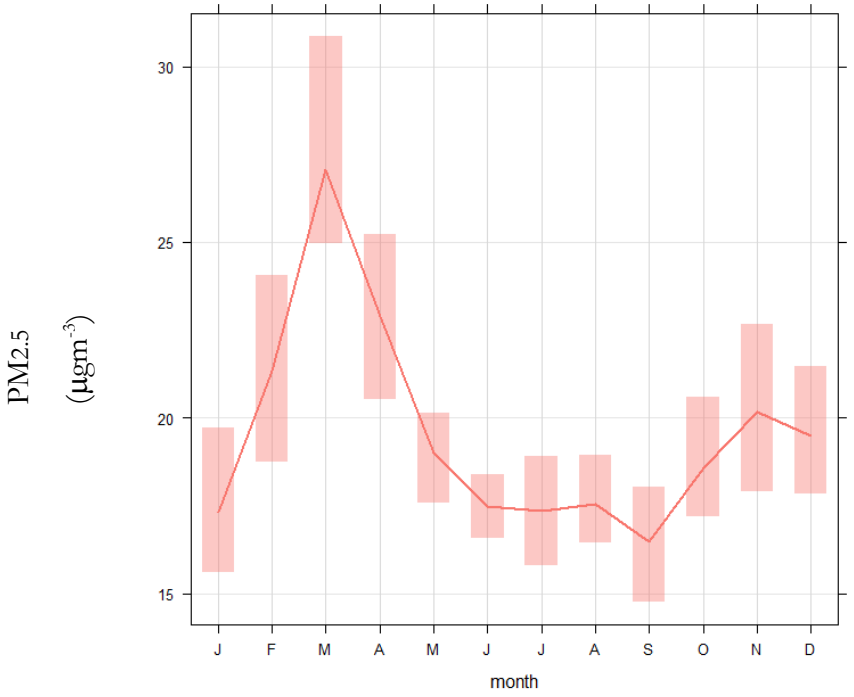



*Figure 3.40* *Monthly variation in PM2.5 concentrations at North Kensington, 2009 – 2012*

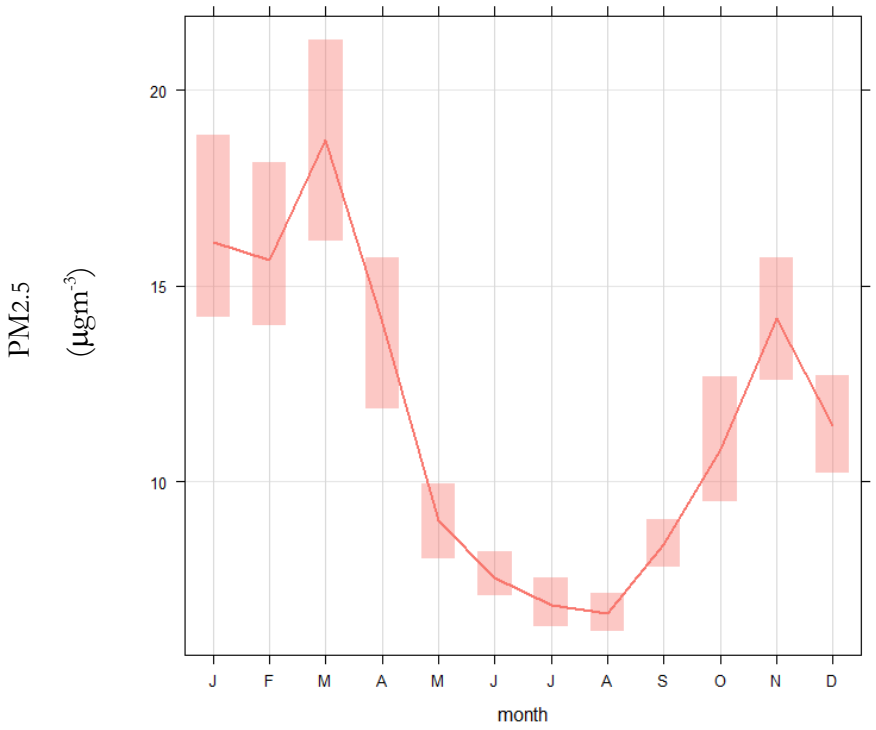


*Figure 3.41* *Monthly variation in PM2.5 concentrations at Marylebone Road, 2002 - 2006*

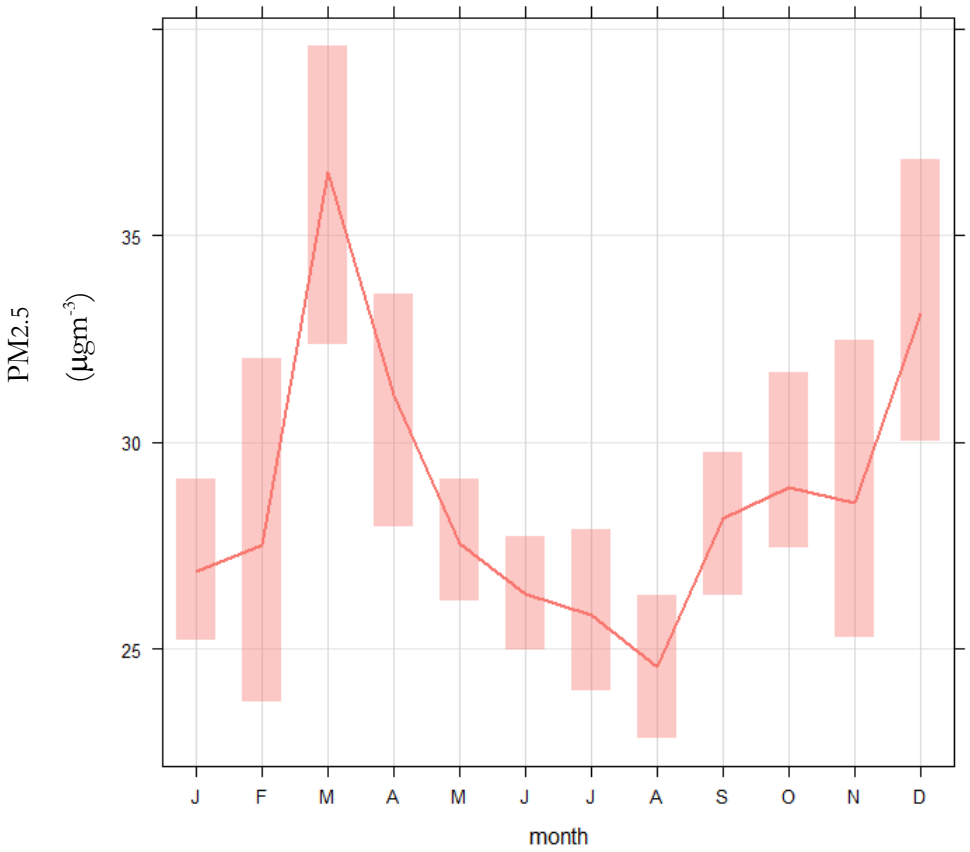
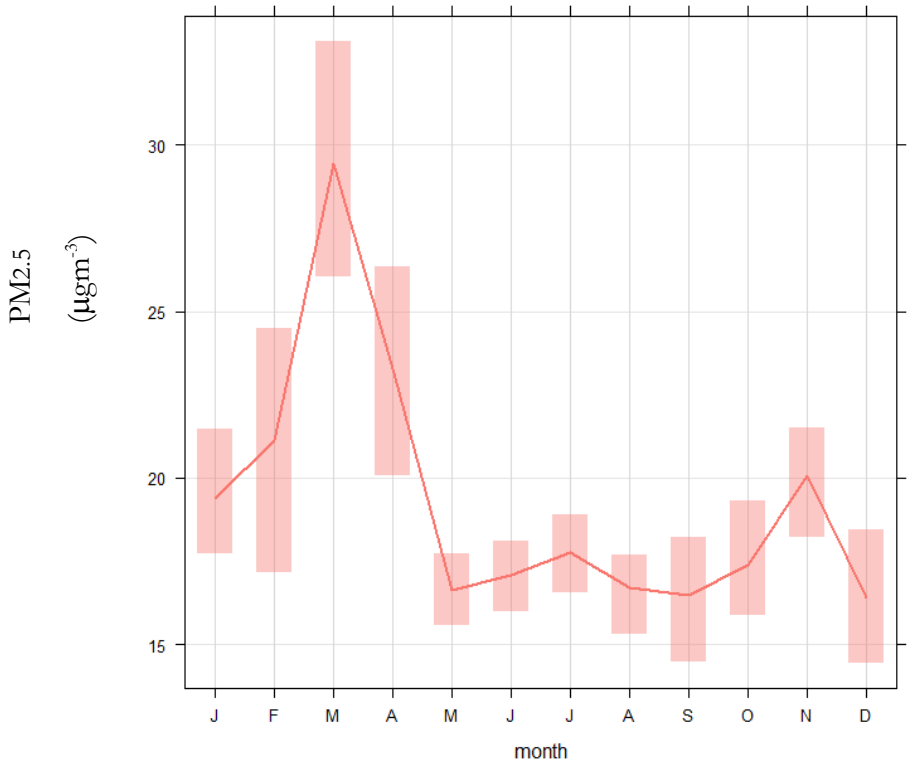


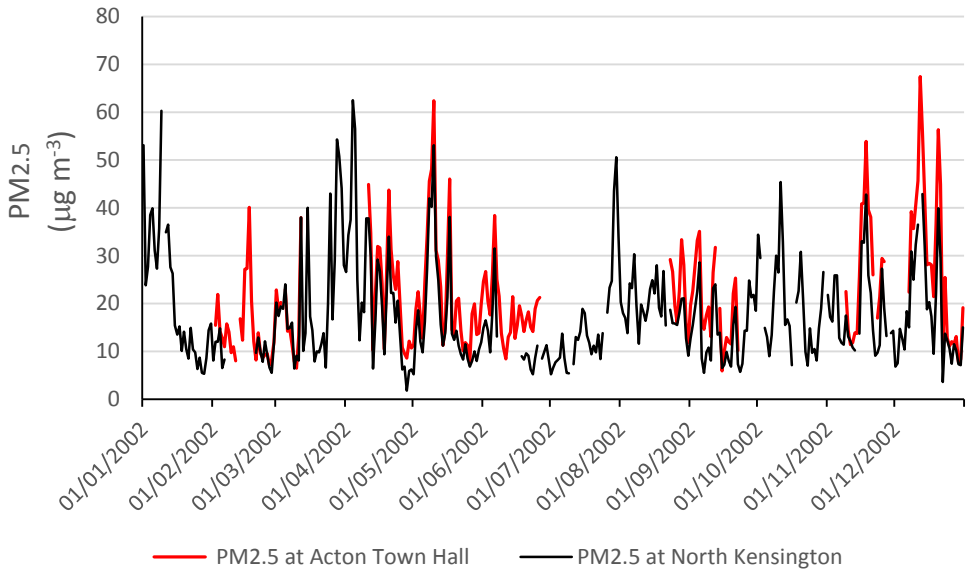

*Figure 3.42* *Monthly variation in PM2.5 concentrations at Marylebone Road, 2009 - 2012*



As for the PM10 concentrations there are distinctive increases in the spring (mainly March) at all sites other than Acton Town Hall. At North Kensington there would seem to be a 40% increase in the concentrations recorded during March over the mean concentration during both periods 2002 – 2006 and 2009 – 2012. The increase is not as high at Marylebone Road – 22% increase in March during 2002 – 2006 and 34 % in March months during 2009 to 2012. However at Acton Town Hall, in March there was a 25% decrease in concentrations, when compared to the annual mean. Some of the causes for these increases are discussed above and further elucidated in chapter 4.

Concentrations between North Kensington in 2002 and Acton Town Hall 2002 were compared in an effort to detect whether there were any differences in concentrations of PM2.5 at the two sites. There were no comparative concentrations for 2001 available. Figure 3.43 compares the time series of North Kensington PM2.5 with Acton Town Hall. As may be seen concentrations at the two sites are very similar, even in the spring months but monitoring did not take place at Acton Town Hall at a time when the concentrations were elevated in April of that year. As already discussed trends in smaller datasets, particularly those with long gaps in the data such as that at Acton Town Hall, need to be treated with some caution but nevertheless will yield useful information in other ways.

*Figure 3.43 North Kensington PM2.5 2002 compared with Acton Town Hall PM2.5 2002*



## *Comparison of $PM_{2.5}$ variation grouped by $PM_{10}$ concentrations*

The mean (arithmetic) $PM_{2.5}$ mass concentrations in each $PM_{10}$ concentration 'bin' determined above might provide some interesting information about the relative contribution of $PM_{2.5}$ to $PM_{10}$ concentrations at the different sites and over time but, as may be seen from the time series data above, there are significant gaps in the $PM_{2.5}$ data at Marylebone Road. It has been decided therefore that a more appropriate comparison for this analysis would be to use only those days where data for both size fractions are available at both Marylebone Road and North Kensington. Details of this smaller dataset are set out in Table 3.10

*Table 3.10 Details of subset of days where PM sampling occurred at both Marylebone Road and North Kensington on the same day ('common days').*

| Site | Sampling period | No of sample days | Arithmetic mean (95% C.I.s) | Arithmetic mean (95% C.I.s) |
|---|---|---|---|---|
| | | | **$PM_{10}$ ($\mu g\ m^{-3}$)** | **$PM_{2.5}$ ($\mu g\ m^{-3}$)** |
| North Kensington | 2002 – 2006 | 1020 | 28.2 (27.3,29.1) | 19.9 (19.1,20.7) |
| Marylebone Road | | | 44.1 (43.0,45.2) | 28.6 (27.7,29.4) |
| | | | | |
| North Kensington | 2009 - 2012 | 690 | 18.5 (17.7,19.4) | 12.0 (11.2,12.7) |
| Marylebone Road | | | 32.9 (31.9,33.9) | 19.2 (18.5,20.0) |

Results of this analysis, including the data from Acton Town Hall, are shown in Figures 3.44 to 3.48 and set out in Table 3.11.

This analysis has yielded some interesting results. At Acton Town Hall and North Kensington as PM10 increased the percentage contribution made by PM2.5 increased such that when PM10 was more than 50 μg $m^{-3}$ the contribution made by PM2.5 was in the region of 80%. At Acton Town Hall the contribution made by the PM2.5 size fraction increased from approximately 60% at low PM10 values (<20 μg $m^{-3}$). The range of the contribution made by the PM2.5 fraction from the lowest 'bin' to the highest 'bin' was narrower at North Kensington in 2002 – 2006 (67% - 82%). The range of the percentage contribution made by the fine fraction at North Kensington between 2009 and 2012 was very similar to Acton Town Hall. This would suggest that at these sites, PM10 concentrations were being driven by PM2.5 concentrations.

However, the situation was different at Marylebone Road where the contribution made by PM2.5 rose with PM10 concentrations but not at the same rate as the other locations and never contributed more than 67% to overall PM10 mass even on high pollution days which was similar to the contribution made at lower PM10 levels by the fine fraction at the other locations. This would suggest that a component of the coarse fraction was more important to increasing PM10 concentrations at Marylebone Road than at the other locations. Additionally it would seem that this component became increasingly important between 2009 and 2012 when compared to the data from North Kensington for the same time period. This would seem to implicate local sources and given the heavily trafficked nature of the location, it would seem reasonable to suggest that this was a fraction related to traffic sources, namely road abrasion together with tyre and brake wear.

*Table 3.11 mean PM2.5 concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentration at each sampling location 2001 - 2012*

| | **PM10 concentration 'bin'** | | | | | |
|---|---|---|---|---|---|---|
| **Site Sampling period** | **<20 (95% C.I)** | **20 – 30 (95% C.I)** | **30 – 40 (95%C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95%C.I.)** | **>60 (95% C.I.)** |
| | **PM2.5 (μg m$^{-3}$)** | | | | | |
| | **Quartz filters** | | | | | |
| Acton Town Hall 2001 – 2002 | 10.0 (9.6,10.5) | 15.7 (15.2,16.2) | 23.9 (23.2,24.6) | 32.2 930.8,33.6) | 39.9 (38.4,41.5) | 56.8 (51.4,62.2) |
| %age contribution to PM10 concentration | 61% | 63% | 69% | 72% | 76% | 78% |
| No of sample days | 84 | 159 | 95 | 37 | 31 | 16 |
| North Kensington 2002 - 2006 | 10.5 (10.1,10.9) | 15.7 (15.4,16.1) | 23.1 (22.3,24.0) | 44.3 (43.7,44.8) | 54.5 (53.4,55.5) | 61.1 (56.9,65.2) |
| %age contribution to PM10 concentration | 67% | 65% | 68% | 77% | 81% | 82% |
| No of sample days | 297 | 388 | 169 | 91 | 32 | 43 |
| Marylebone Road 2002 - 2006 | 9.7 (8.6,10.8) | 15.5 (15.0,16.1) | 22.0 (21.5,22.5) | 29.1 (28.4,29.8) | 35.6 (34.5,36.7) | 52.0 (49.4,54.4) |
| %age contribution to PM10 concentration | 59% | 62% | 63% | 65% | 66% | 67% |
| No of sample days | 23 | 173 | 287 | 250 | 137 | 150 |
| | **Emfab™ filters** | | | | | |
| North Kensington 2009 - 2012 | 7.3 (7.0,7.5) | 15.4 (14.7,16.2) | 24.7 (23.1,26.3) | 33.9 (32.0,35.8) | 41.2 (37.3,45.0) | 53.2 (49.2,57.2) |
| %age contribution to PM10 concentration | 57% | 66% | 73% | 78% | 76% | 81% |
| No of sample days | 479 | 126 | 39 | 22 | 13 | 11 |
| Marylebone Road 2009 - 2012 | 8.8 (8.1,9.4) | 14.7 (14.2,15.3) | 19.6 (19.0,20.2) | 24.6 (23.3,25.9) | 30.2 (27.8,32.7) | 45.1 (40.6,50.0) |
| %age contribution to PM10 concentration | 58% | 59% | 57% | 56% | 56% | 66% |
| No of sample days | 102 | 192 | 232 | 91 | 36 | 37 |

*Figure 3.44 mean PM2.5 concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentration at Acton Town Hall, 2001 - 2002*

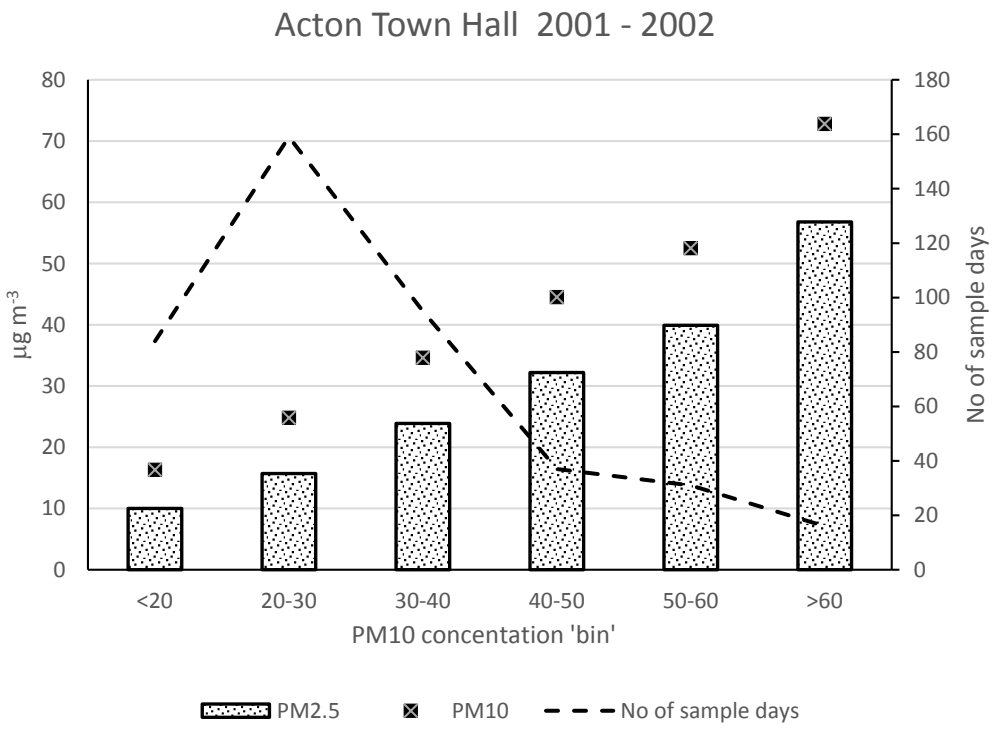


*Figure 3.45* *mean PM2.5 concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentration at North Kensington, 2002 – 2006 (common days)*

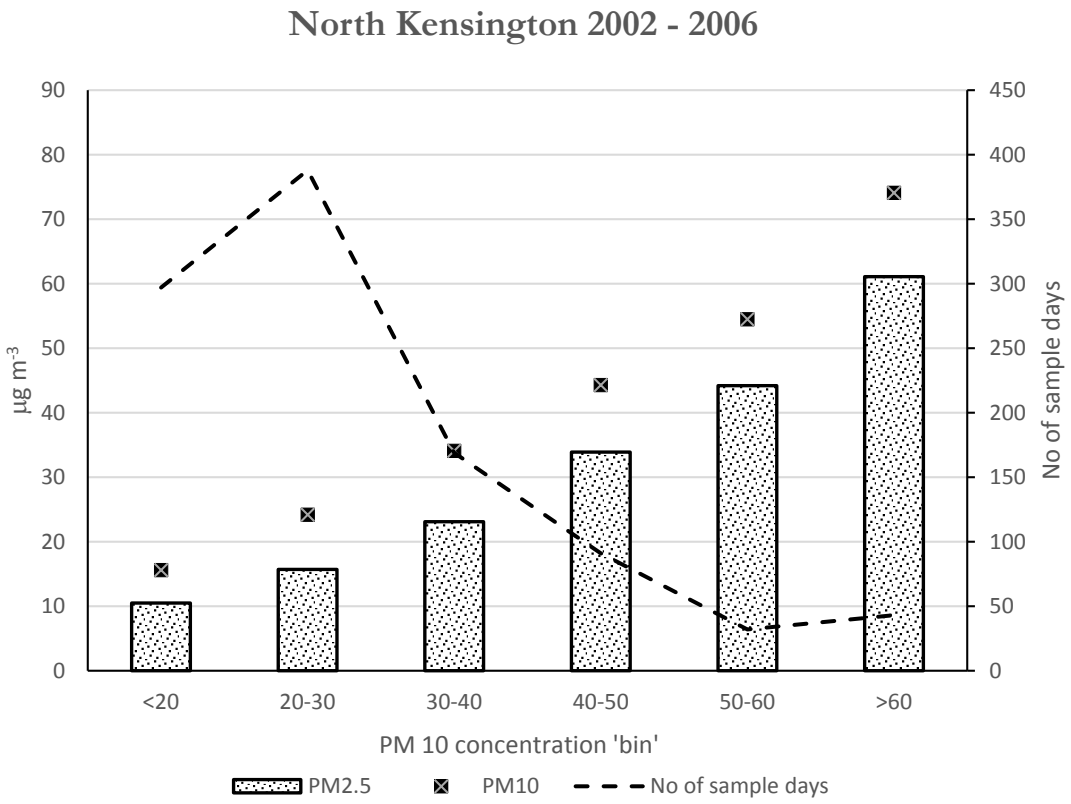



*Figure 3.46* *mean PM2.5 concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentration at Marylebone Road, 2002 – 2006 (common days)*

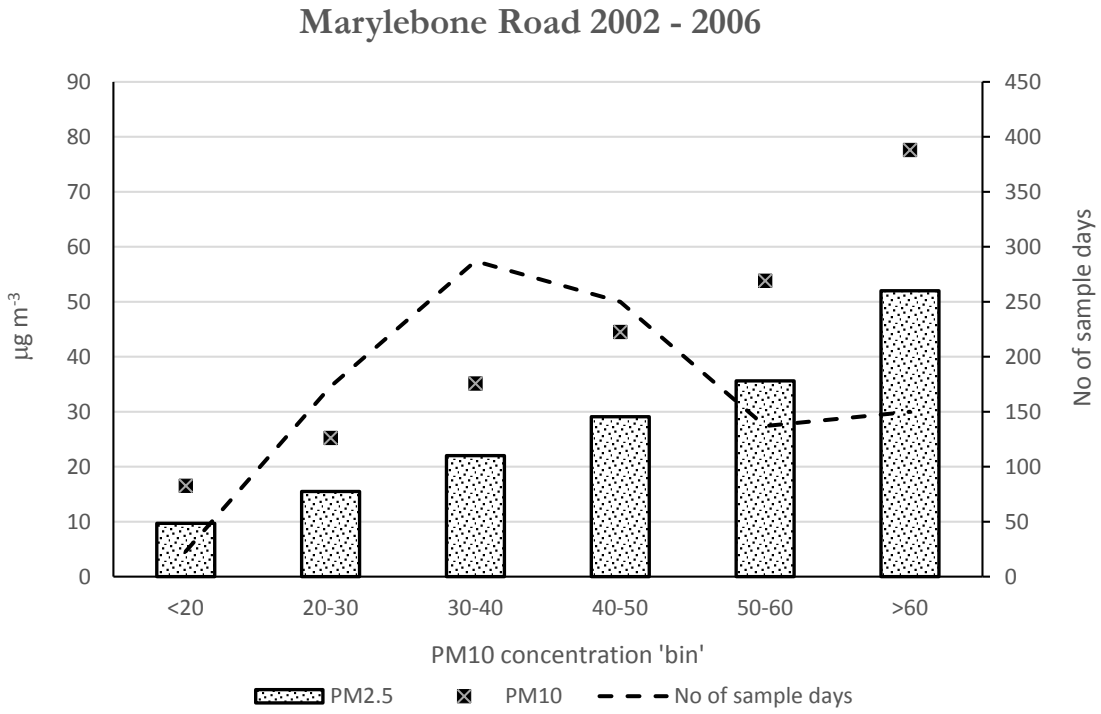


*Figure 3.47* *mean PM2.5 concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentration at North Kensington, 2009 – 2012 (common days)*

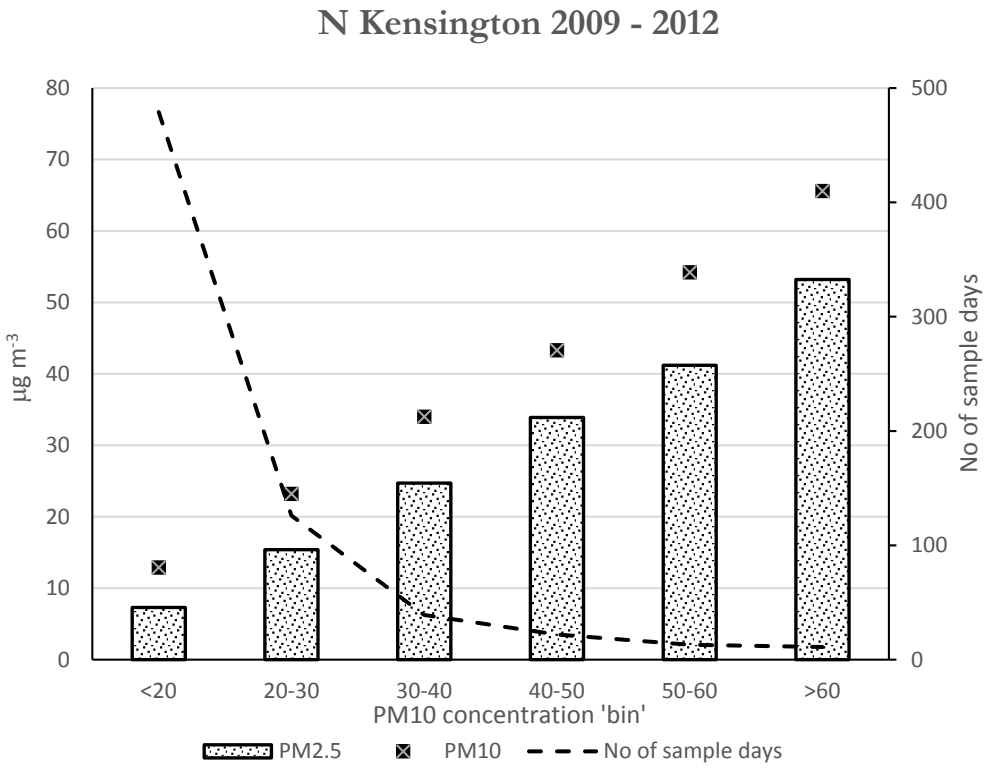
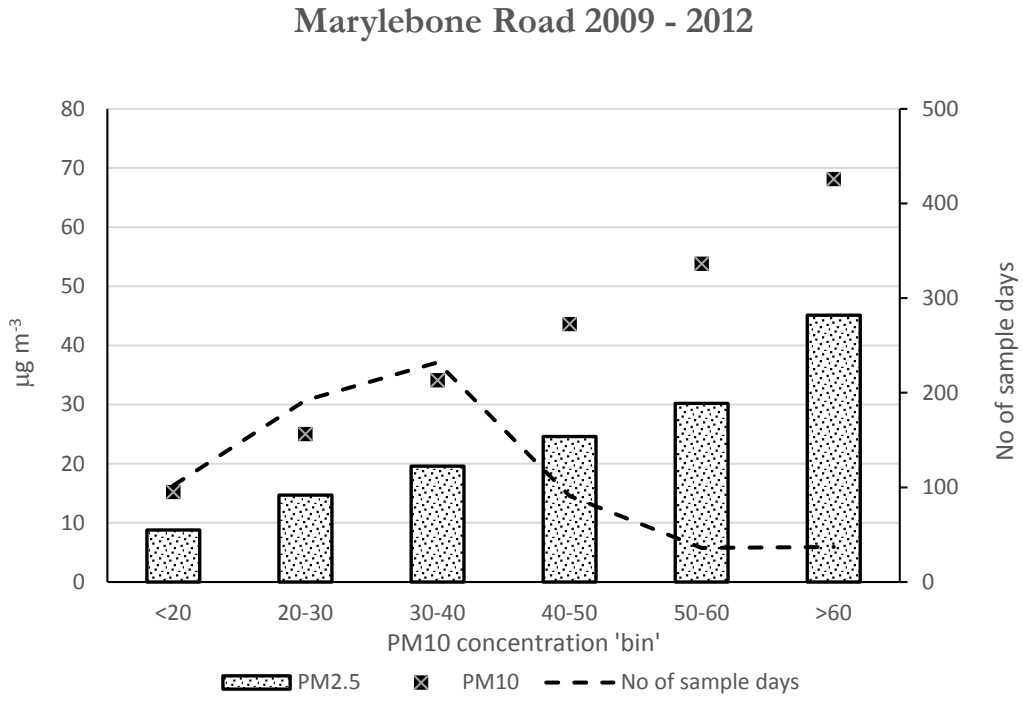



*Figure 3.48* *mean PM2.5 concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentration at Marylebone Road, 2009 – 2012 (common days)*



# Summary

The choice of sampling locations has provided a range of locations in London from an urban background site at North Kensington, a suburban site in west London and two busy trafficked highways in London. It is a strength of this study that the orientation of the sites, other than the background site, are similar and therefore meteorological conditions and influences would have been very similar. As discussed in chapter 2, there are uncertainties associated with the various sampling methods but all of the concentrations used in this analysis were derived from the sampling method (Partisol sampler) and therefore the underlying uncertainties would have been similar. Concentrations of $PM_{10}$ and $PM_{2.5}$ were consistent with the conceptual model suggested by Lenschow et al. (2001) with an increment in PM concentrations from background to kerb / roadside.

Differences in concentrations measured using different filter substrates before and after 2007 has meant that the time series of data at both North Kensington and Marylebone Road have been treated as two different populations but this has resulted in being able to draw out different developments in PM concentrations at the two sites.

Trend analysis suggests that there were increasing trends in $PM_{10}$ and $PM_{2.5}$ concentrations at North Kensington and Marylebone Road between 2002 and 2006. A similar trend was discernible at Acton Town Hall between 2001 and 2002 but needs to be treated with more caution as there are long time periods where no monitoring took place. However this trend was not discernible at North Kensington, Marylebone Road or Oxford Street between 2009 and 2012. At each of these sites PM concentrations appear to have remained static during this period.

Monthly differences were noticeable at all of the sites. Peaks in concentrations in March were noticeable at North Kensington, Marylebone Road and Oxford Street which is attributed (see, e.g., Harrison, 2012) to springtime elevations in secondary sources from the near continent. This springtime behaviour was not discernible in the data from Acton Town Hall but closer investigations suggests that this was simply due to insufficient data at the appropriate times. This seasonal phenomenon is further explored in chapter 4.

The distribution of PM10 concentrations varied from site to site. On the majority of days at North Kensington and Acton Town Hall, PM concentrations were below 30 μg $m^{-3}$ but this was not the case at either Marylebone Road or Oxford Street. At these sites PM10 concentrations were more often close to or above the Daily Limit Value.

Consideration of days when the Daily Limit Value of 50 μg $m^{-3}$ yields some interesting differences between the different sampling locations. Between 2001 and 2006 more than 10% of sample days were above the Daily Limit Value at all the kerb/roadside sampling locations (at North Kensington during 2002 and 2004 only 4% of days were above the Daily Limit Value). Indeed, at Marylebone Road the percentage number of days above the Daily Limit Value ranged from 22% (2004) to 38% (2006). There was a marked reduction in the number of days above the Daily Limit Value between 2009 and 2012 but it is not clear how much of this may be attributed to the change of sampling filter substrate and how much was a result of real reductions in concentrations. Perhaps even more interestingly it is generally accepted that episodic peaks in PM concentrations are mainly driven by a greater increase in particles in the fine fraction, mainly from regional sources, and this would seem to have been the case at Acton Town Hall and North Kensington. It was not however the case at Marylebone Road. Here, increases in the coarse fraction seemed to have an equal influence on rising PM concentrations. Whilst it is difficult to be certain as to the cause for this, based simply on PM concentrations, it seems likely that this was due to local influences suggesting road abrasion together with brake and tyre wear must be at least a contributory factor.

Despite an accumulation of initiatives in London which might have been expected to produce reducing concentrations, it would appear from gravimetric measurements that no real overall reductions in PM mass concentrations have been achieved at the sampling locations. Discerning longer term trends is however confounded by changes in filter substrate. This change has important implications and it is not possible to determine if policies have been efficacious. However, ambient PM is a mixture and it may be that these initiatives have influenced contributory components to airborne PM in different ways.

In the following chapters, the contribution to overall PM10 concentrations made by secondary and primary sources are considered and compared in more detail

# Chapter 4

# Assessing the contribution of inorganic sources to $PM_{10}$ concentrations in London 2001 - 2012

## Introduction

It is recognised that the principal inorganic sources contributing to $PM_{10}$ concentrations are ammonium nitrate ($NH_4NO_3$), ammonium sulphate ($(NH_4)_2SO_4$) and sodium chloride (NaCl) (see for example AQEG, 2005 and AQEG, 2012). Ammonium nitrate and ammonium sulphate are, as discussed in chapter 1, key indicators of the secondary component in $PM_{10}$ concentrations. Sodium chloride is mainly expected to be present as sea-salt, which is not influenced by human activity and therefore may be a key indicator of natural sources. Ion chromatography has been used to determine the inorganic anions: sulphate (as $SO_4^{2-}$), nitrate (as $NO_3^-$) and chloride (as $Cl^-$) in $PM_{10}$ concentrations collected on $PM_{10}$ filter samples using Partisol 2025 samplers at North Kensington and Marylebone Road between 2002 and 2012 as part of Defra's Airborne Particulate Concentrations and Numbers in the UK (Contract Reference CPEA 28) operated by NPL and ERG at KCL. Summaries of the programme are contained in several peer reviewed publications and in a series of annual reports (see for example Abdalmogith and Harrison, 2006, Beccaceci et al., 2013). Details of these concentrations are available via the Defra UK-AIR website (air-uk.defra.gov.uk).

Ion chromatography was also used in this project to determine the same inorganic anions in PM10 collected as part of the sampling programme at Acton Town Hall during 2001 and 2002. Details of that analysis are provided in chapter 2.

Initially, to estimate a mass concentration due to these anions, a balancing cation has been used based on the assumption that anions are in the form of ammonium nitrate, ammonium sulphate and sodium chloride as set out in chapter 2. For this analysis the anion concentrations measured on the coarse and fine filters at Acton Town Hall have been combined to provide a total concentration of each species. Harrison et al. (2003) proposed a pragmatic mass closure model and suggested that both ammonium nitrate and ammonium sulphate mass concentration should be increased by a factor of 1.29 to allow for strongly bound water associated with each species. Other schemes have been suggested including that of Frank (2006) who suggested a factor of 0.24 applied to the mass concentration of ammonium and sulphate. No correction for particle bound water was undertaken in this study and should be borne in mind when making comparisons with other studies which may have included such a factor.

Trends in anion concentrations during the period 2001 – 2012 at each site are discussed in order to consider whether these have altered over time. Measurements are available at North Kensington and Marylebone Road over the same time period and only those days which have measurements at each site have been used to consider and compare the contribution made by each species to PM10 concentrations. Additionally, to compare anion concentrations of overall PM10 concentrations the datasets have been further sub-divided between 2002 to 2006 and 2009 and 2011 (no measurements are available for North Kensington for 2012), reflecting the change in filter substrate for gravimetric measurements. It should also be noted that sodium chloride measurements were not available from Marylebone Road for 2010. Each species is considered separately.

Finally, nitrate may not entirely be present in PM10 as ammonium nitrate. It also occurs as sodium nitrate in the coarse fraction (Harrison et al. 2003, 2004). Similarly not all of the chloride may be present as sea salt (White, 2008). It is possible to explore the contribution of these species to the different PM size fractions measured at Acton Town Hall and the interpretation of the concentrations at North Kensington and Marylebone Road have been further considered in this context.

# Results and Discussion

It is important to bear in mind that different numbers of sample days have been used throughout this analysis in respect of Marylebone Road and North Kensington (but not Acton Town Hall). There were a number of days when anion analysis took place but PM10 mass concentration measured gravimetrically did not. Additionally not all three species were reported for all the same days at Marylebone Road and North Kensington, leading to what at first would seem to be discrepancies in total number of sample days but is actually a reflection of data availability.

## AMMONIUM SULPHATE

Figures 4.1 – 4.3 are the time series graphs for ammonium sulphate concentrations at the three sites and Table 4.1 sets out the mean and maximum concentrations. There is clearly a lot of day to day variation in concentrations but overall the mean concentrations (Table 4.1) are very similar. The date with maximum concentrations at both Acton Town Hall and North Kensington was the same (10 May 2002) despite the much longer timescale of the latter dataset (2002 – 2011). No concentrations were reported for Marylebone Road on that date.

*Table 4.1 Mean and maximum concentrations of ammonium sulphate at the study sites*

| Site | Sampling period | No of sample days | ammonium sulphate ($\mu g\ m^{-3}$) | |
|---|---|---|---|---|
| | | | Mean (95%C.I.'s) | Maximum (date) |
| Acton Town Hall | January 2001 – December 2002 | 404 | 4.2 (3.9,4.4) | 25.2 (10.5.02) |
| North Kensington | 2002 – 2011 | 3118 | 3.7 (3.6,3.8) | 28.5 (10.5.02) |
| Marylebone Road | 2002 - 2012 | 2826 | 4.0 (3.9,4.1) | 23,1 (16.9.06) |

*Figure 4.1* *Time series of ammonium sulphate concentrations, Acton Town Hall, 2001 - 2002*

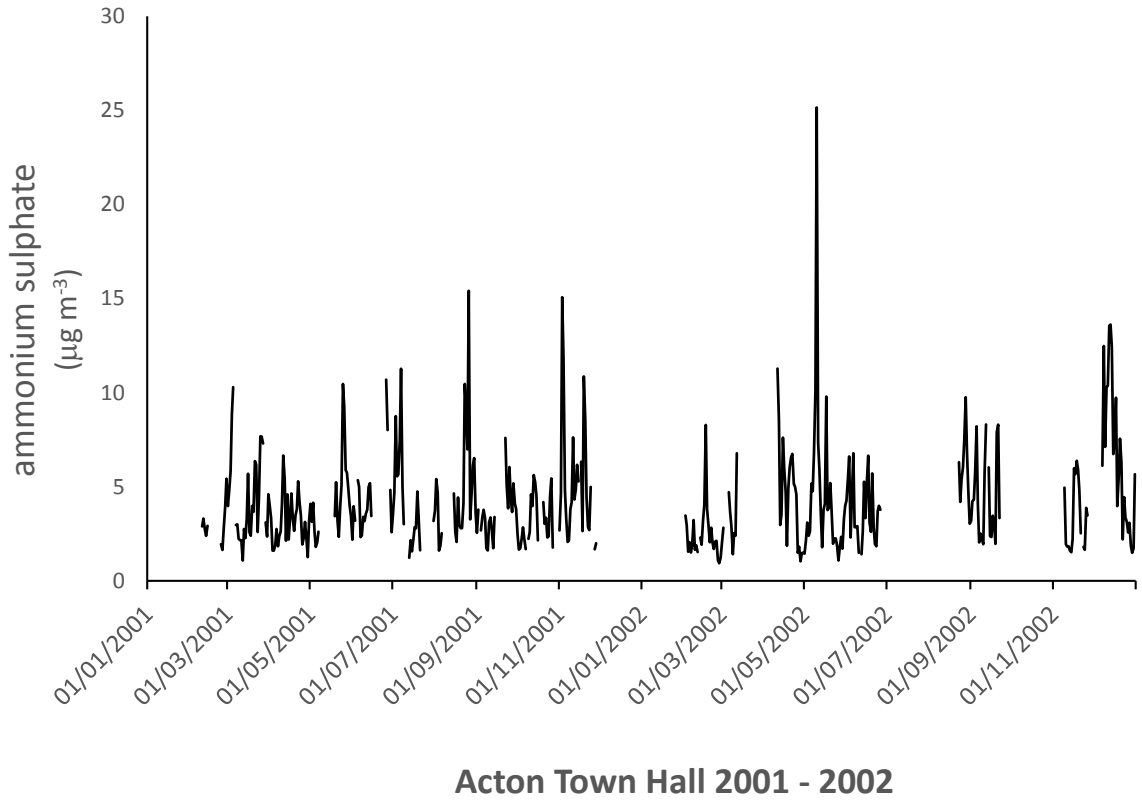


*Figure 4.2* *Time series of ammonium sulphate concentrations, North Kensington, 2002 - 2011*

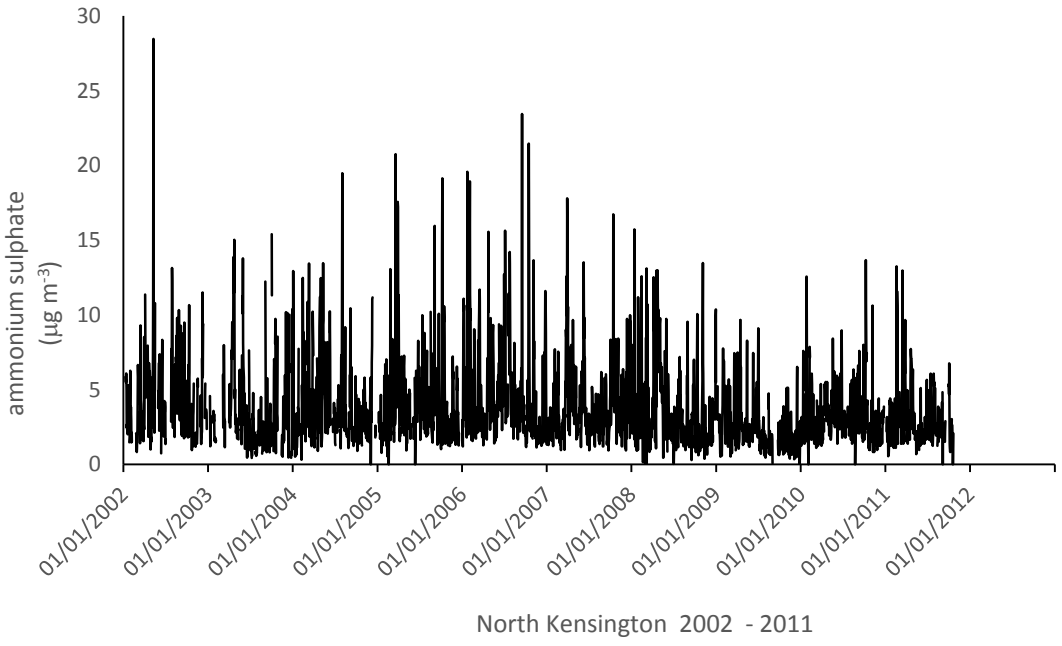
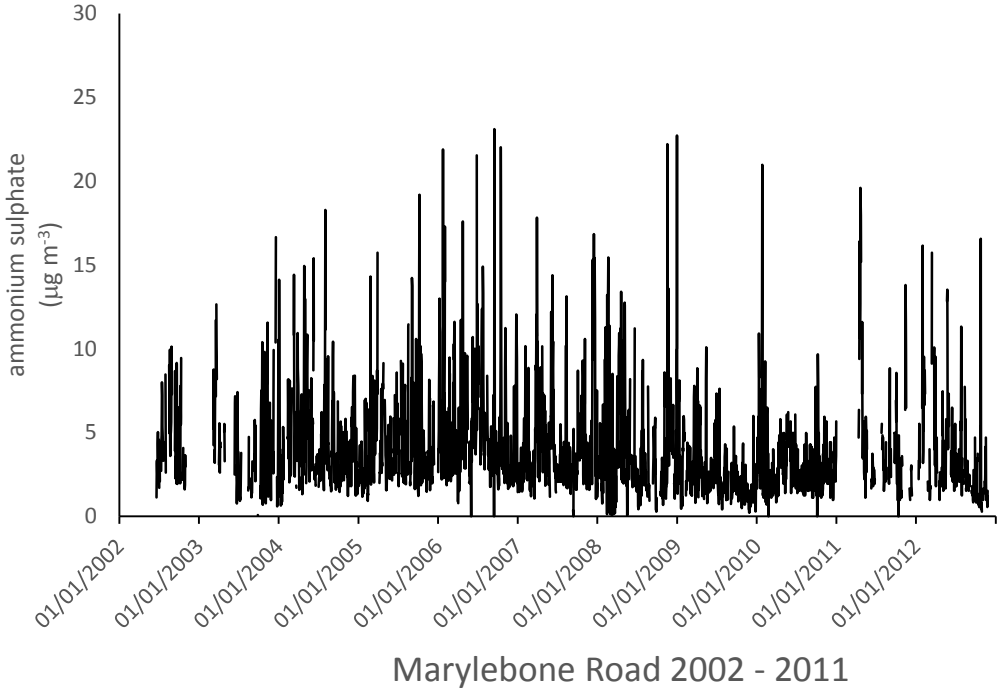



*Figure 4.3* *Time series of ammonium sulphate concentrations, Marylebone Road, 2002 – 2012*



## *Trend Analysis (ammonium sulphate)*

Trend analysis using the TheilSen function in Openair (Carslaw and Ropkins, 2012) is shown in Figures 4.4 to 4.6. It is apparent that the trend at Acton Town Hall is different from those at North Kensington and Marylebone Road which measured over the longer timescales. There is a clear and significant decreasing trend at both North Kensington and Marylebone Road from 2002 – 2011. Details of the trends are set out in Table 4.2 along with their statistical significance. In both cases 95% confidence intervals reported for North Kensington and Marylebone Road are also negative and along with p values of <0.001 it can be stated with confidence that reductions have been achieved.

*Table 4.2* *Summary of TheilSen trend analysis and statistical significance, ammonium sulphate, Acton Town Hall, 2001 – 2002, North Kensington 2002 – 2011, Marylebone Road 2002 – 2012*

| ammonium sulphate | | | | |
|---|---|---|---|---|
| **Site** | **Sampling period** | **No of sample days** | **trend (μg m$^{-3}$) per year (95% C.I.)** | **p** |
| Acton Town Hall | 2001 – 2002 | 404 | 0.53 (-0.32, 1.42) | >0.1 |
| North Kensington | 2002 - 2011 | 3114 | -0.19 (-0.28,-0.09) | <0.001 |
| Marylebone Road | 2002 - 2012 | 2826 | -0.17 (-0.25,-0.09) | <0.001 |

Jones and Harrison (2011) report a non-significant upward trend at North Kensington (0.001 μg m$^{-3}$ yr$^{-1}$) in sulphate concentrations for the period 1996 to 2008 but a significant downward trend at Marylebone Road (-0.08 μg m$^{-3}$ yr$^{-1}$) between 1997 and 2008.

It is worth considering both the time series and the monthly means demonstrated on the trend graphs, particularly North Kensington, in more detail. There would appear to be a noticeable step change in concentrations in the spring of 2008 which was also noted by AQEG (2012) and Jones et al. (2011). The cumulative sum technique (Barratt et al., 2007) was used by Jones et al. (2011) to identify change points in relation to particle number concentrations and found reductions between 30 and 50% in mean concentrations between 2008 and 2009. Ultra-low sulphur fuel for all vehicles was introduced at the beginning of 2008 in the UK and the first phase of the Low Emission Zone in London was implemented from February 2008 and the second phase from July 2008. Jones et al. (2012) consider that both these initiatives might have led to the reduction in both particle number and ammonium sulphate concentrations with greater likelihood of the change being due to the fuel change.

*Figure 4.4* *TheilSen analysis, ammonium sulphate, Acton Town Hall 2001 - 2002*

**(p >0.1**)

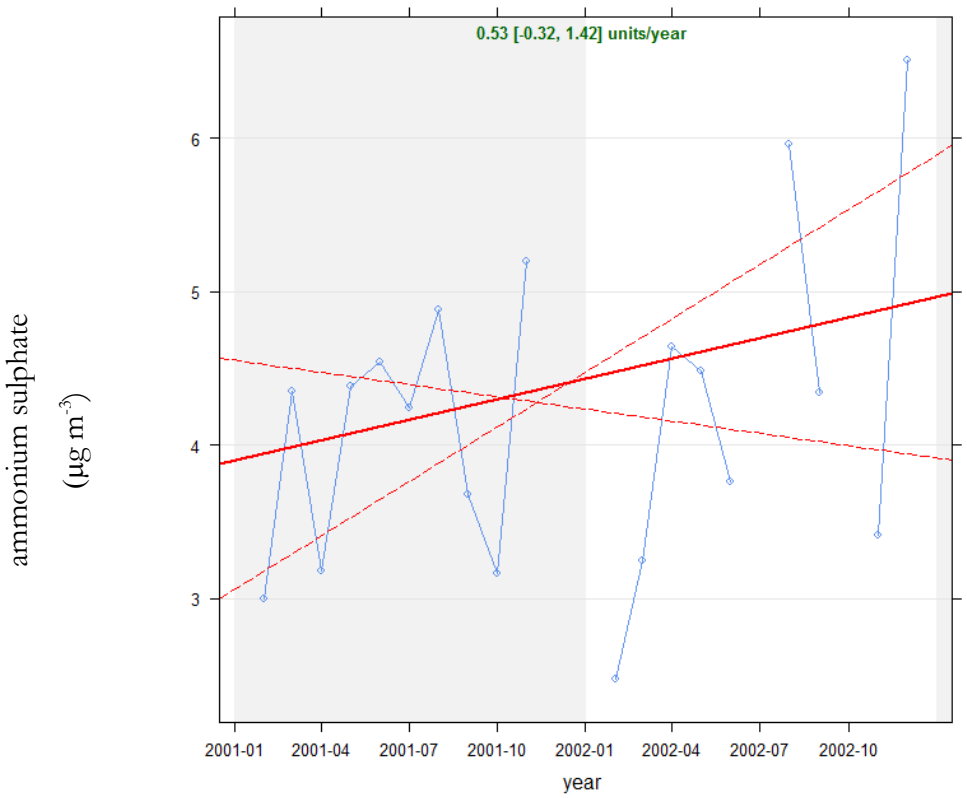


*Figure 4.5* *TheilSen analysis, ammonium sulphate, Marylebone Road, 2002 – 2012 (p = <0.001)*

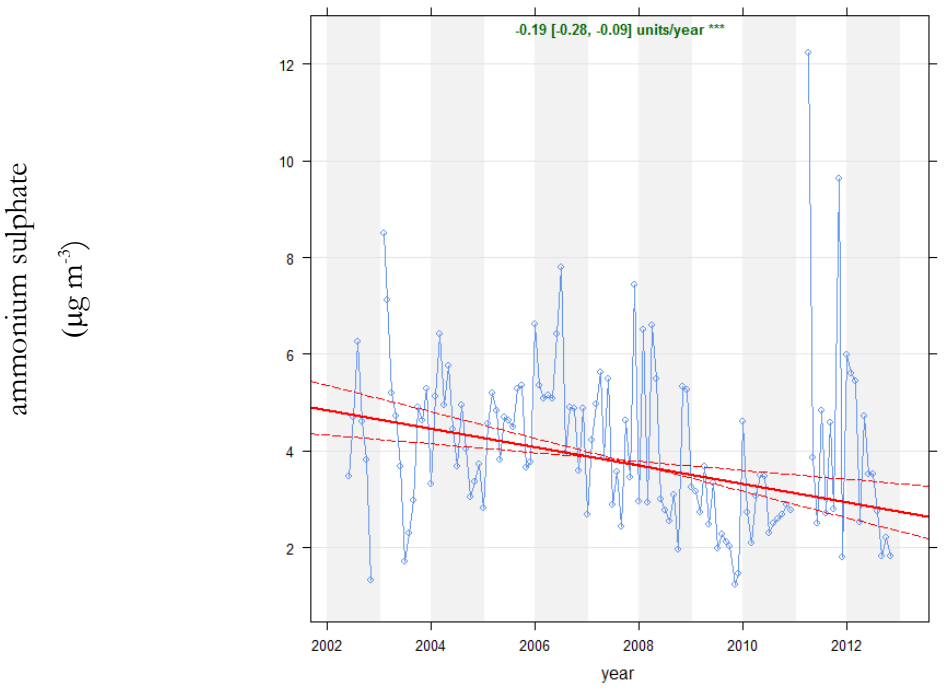
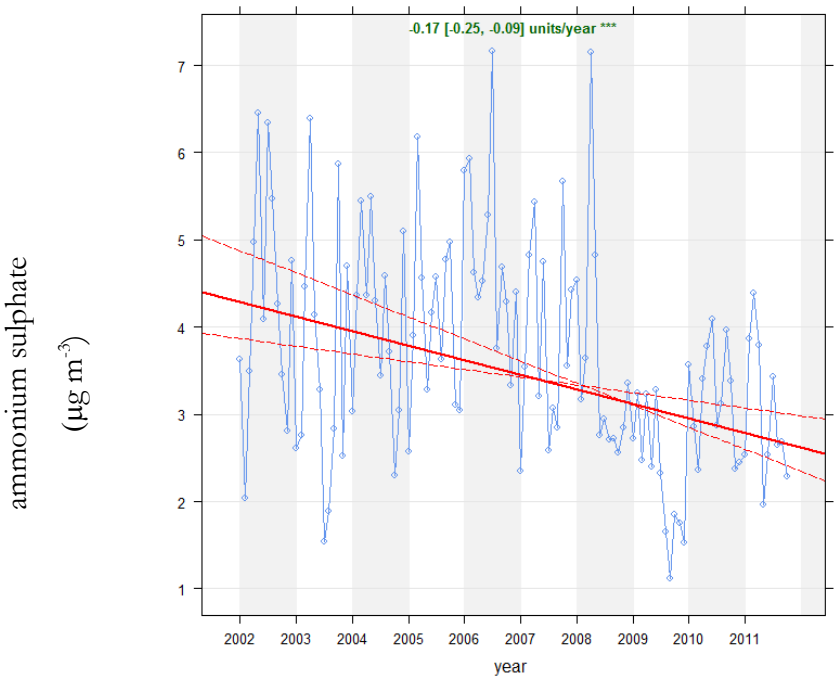



*Figure 4.6* *TheilSen analysis, ammonium sulphate, North Kensington, 2002 – 2011 (p <0.001)*



In order to consider the trends in ammonium sulphate in more detail, three subsets of both the Marylebone Road and the North Kensington datasets for the periods:

2002 – 2006, 2007 – 2008 and 2009 – 2011 (2009 to 2012 at Marylebone Road)

were chosen to carry out separate trend analysis to consider whether different trends were discernible both before and after the apparent reduction in concentrations in 2008. The results are set out in Table 4.3. None of the trends are significant at $p<0.1$ but they all show similar trends for the appropriate time period. Between 2002 and 2006 there was an upward trend, followed by a downward trend in 2007 and 2008 and then a return to an upward trend after 2009. Mean concentrations for each time period are also shown in Table 4.3. There was a progressive reduction in mean concentrations across the time periods at each site. At North Kensington mean concentrations were 4.2 $\mu g\ m^{-3}$ during 2002 – 2006. There was a 30% reduction in concentrations such that between 2009 and 2011 mean mass concentrations were 2.9 $\mu g\ m^{-3}$. A similar pattern emerged at Marylebone Road between 2002 / 2006 and 2009/2012 with respective mean mass concentrations of 4.7 $\mu g\ m^{-3}$ and 3.1 $\mu g\ m^{-3}$. Clearly there has been a fall in concentrations of ammonium sulphate which has not been sustained and the elimination of sulphur in vehicle fuel seems the most likely candidate. The return to an increasing trend may be due to more regional sources, for example from electricity generation in the Thames Estuary (although Kingsnorth power station in Kent has since ceased operation in 2012), non-UK sources or increases in the dieselisation of the UK traffic fleet.

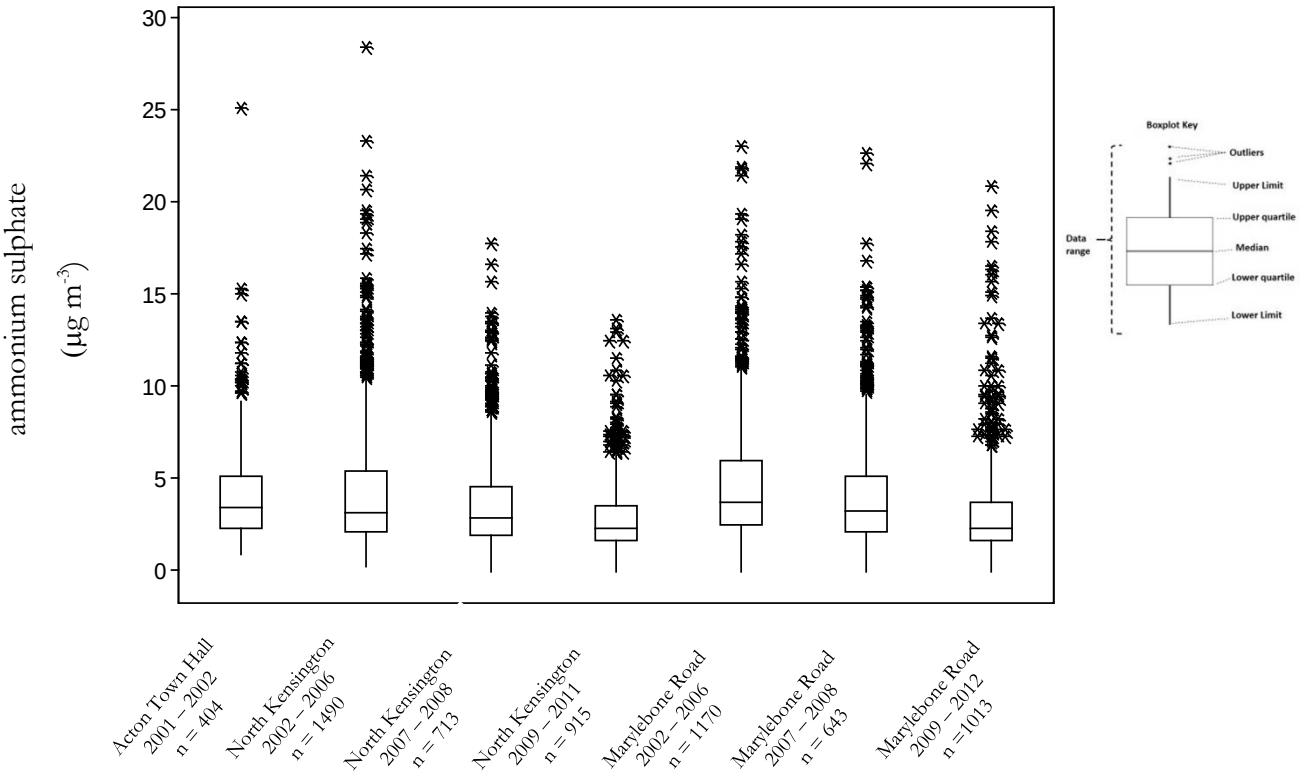
*Table 4.3 Summary of TheilSen trend analysis and statistical significance: ammonium sulphate at North Kensington and Marylebone Road, 2002 – 2006, 2007 – 2008 and 2009 - 2012*

| Sampling period | Site | No of sample days | Overall trend ($\mu g\ m^{-3}$) per year (95% C.I.) | p | Mean (95%C.I.) |
|---|---|---|---|---|---|
| 2002 -2006 | North Kensington | 1490 | 0.14 (-0.06,0.38) | >0.1 | 4.2 (4.1,4.4) |
| | Marylebone Road | 1170 | 0.13 (-0.08,0.48) | >0.1 | 4.7 (4.5,4.8) |
| | | | | | |
| 2007 - 2008 | North Kensington | 713 | -0.37 (-1.44,0.63) | >0.1 | 3.7 (3.5,3.9) |
| | Marylebone Road | 643 | -0.37 (-1.44,0.63) | >0.1 | 4.3 (4.0,4.5) |
| | | | | | |
| 2009 - 2011 | North Kensington | 915 | 0.19 (-0.04,0.6) | >0.1 | 2.9 (2.8,3.0) |
| 2009 - 2012 | Marylebone Road | 1013 | 0.16 (-0.14,0.57) | >0.1 | 3.1 (2.9,3.2) |

Figure 4.7 is boxplots of the concentrations of ammonium sulphate at each site and separated into the same time periods. The overall decrease in concentrations is also apparent in these plots.

The mean concentration at Acton Town Hall was 4.2 (± 0.27) μg $m^{-3}$.

*Figure 4.7 Box plots comparing concentrations (μg $m^{-3}$) of ammonium sulphate*



## *Day of the week and Monthly Trends (ammonium sulphate)*

Day of the week trends at each site are shown in Figures 4.8 to 4.12. Given the apparent step change in concentrations the data at each site have been analysed for the two time periods 2002 to 2006 and after 2009. At Acton Town Hall between 2001 and 2002 there was very little variation between day of week concentrations in ammonium sulphate concentrations with wide 95% confidence limits. There is a similar pattern at North Kensington and Marylebone Road for the period 2002 to 2006.

The patterns in daily concentrations at North Kensington and Marylebone Road after 2009 demonstrate different day of week behaviour to those between 2002 and 2006. Interestingly, there were small concentration reductions on Saturdays and Sundays at both sites in the region of 12% when compared with weekday concentrations. Bearing in mind that there are overall reductions in mass concentrations as well, this suggests that there were local reductions brought about by changes in traffic emissions. The appearance of this day of week behaviour coincided with the change in sulphur fuel content and it seems possible to conclude that the two events are connected. This however seems to contradict the expected outcome from a decrease in sulphate from traffic. However it is also interesting that the downward trend was not gradual. It occurred over a very short timescale, quickly reverting to an increasing one suggesting perhaps that regional sources were not declining in the same way.

In the next section, the monthly mass concentrations during 2002 and 2006 and 2009 to 2012 at North Kensington and Marylebone are considered separately to ascertain whether these reductions have varying seasonal effects.

*Figure 4.8 Day of the week variation in ammonium sulphate concentrations, Acton Town Hall, 2001 - 2002*

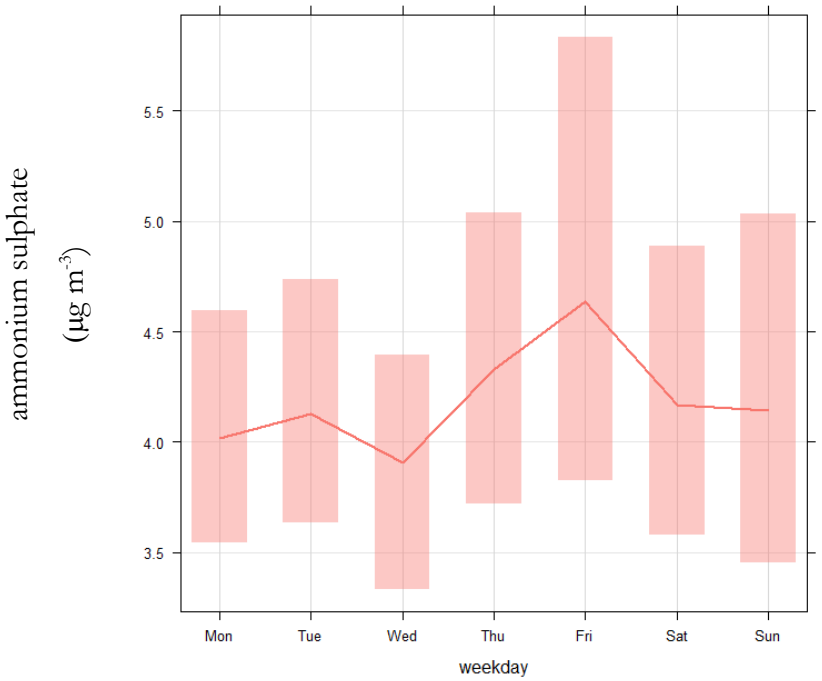


*Figure 4.9 Day of the week variation in ammonium sulphate concentrations, Marylebone Road, 2002 - 2006*

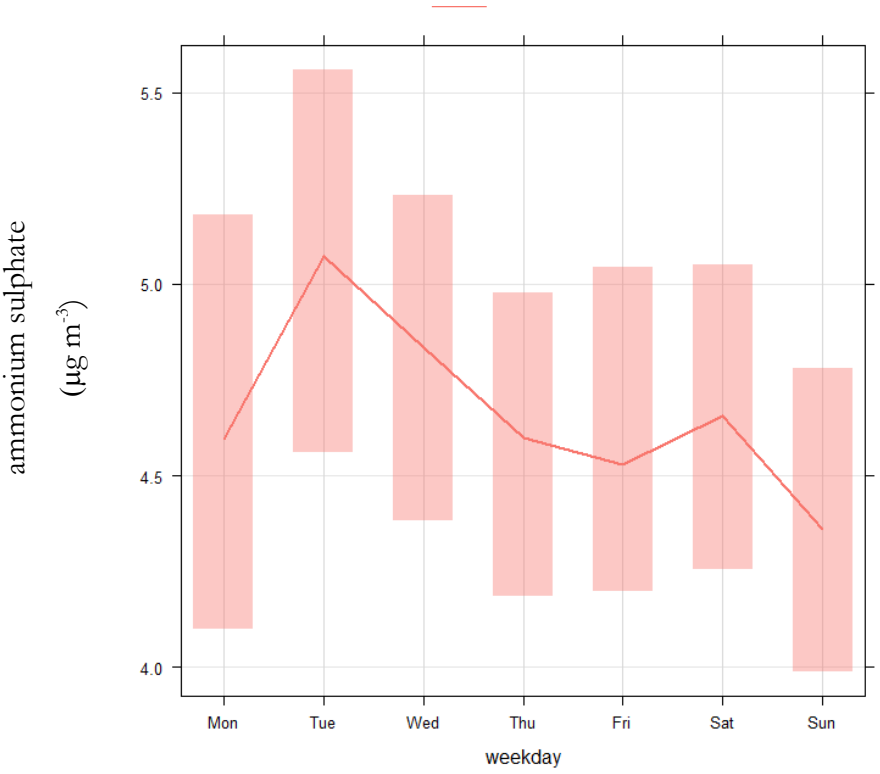



*Figure 4.10 Day of the week variation in ammonium sulphate concentrations, Marylebone Road, 2009 - 2012*

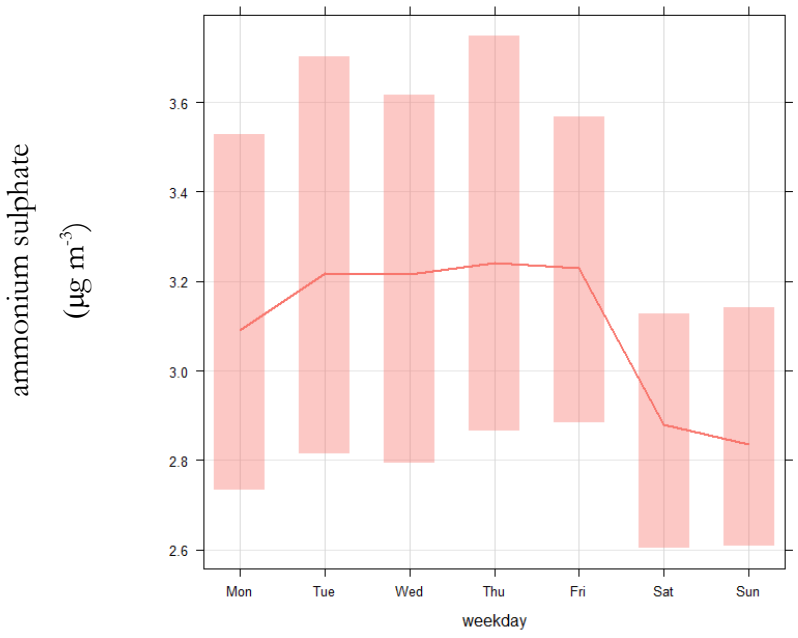


*Figure 4.11 Day of the week variation in ammonium sulphate concentrations, North Kensington, 2002 – 2006*

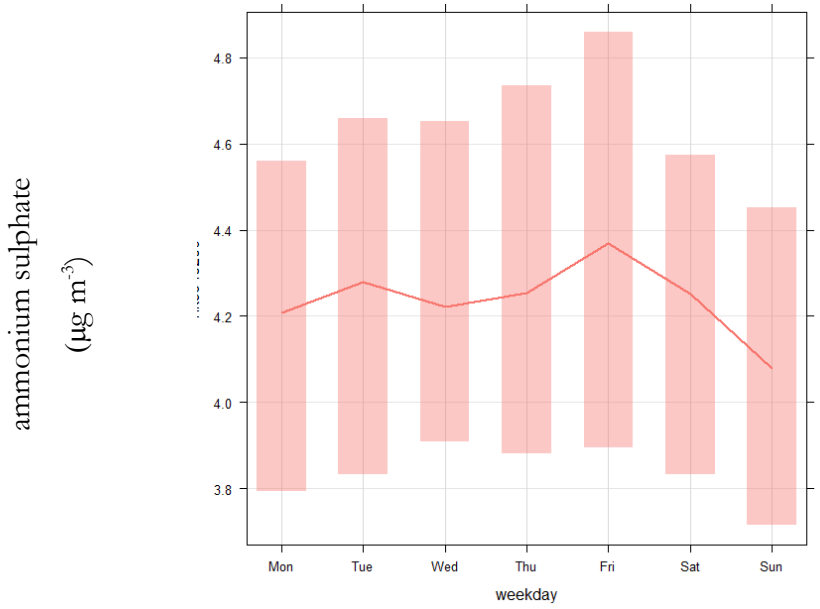
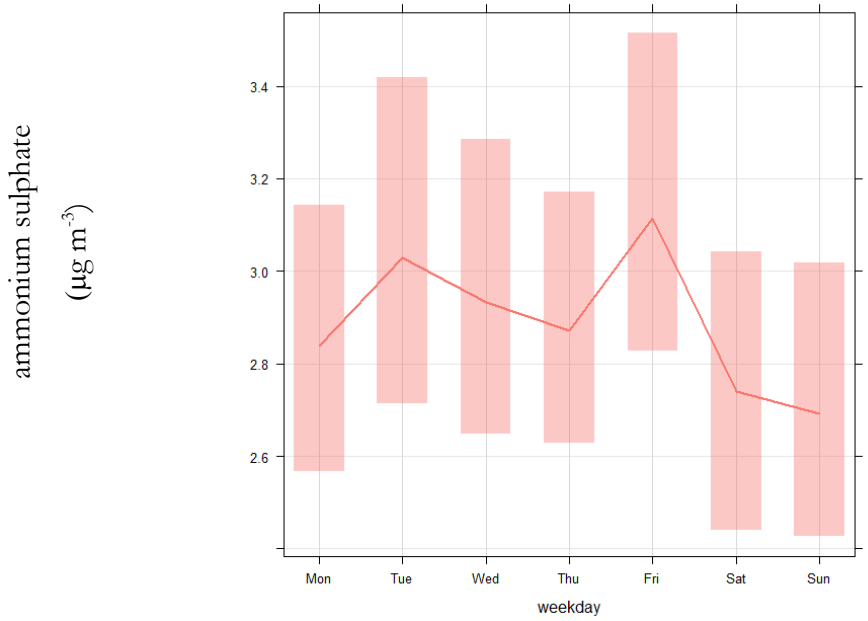



*Figure 4.12 Day of the week variation in ammonium sulphate concentrations, North Kensington, 2009 – 2011*



Monthly variation at each site is illustrated in Figures 4.13 to 4.17 and details of the mass concentrations are set out in Table 4.4. AQEG (2012) noted that the greatest concentrations of sulphate in the UK between 1999 and 2009 were in March and April with higher concentrations extending through the summer months. This pattern was clear at both Marylebone Road and North Kensington during the period 2002 to 2006 but not at Acton Town Hall, where the highest concentrations were recorded in December. However, as noted in chapter 3 this may be due to monitoring not occurring during spring episodes in both 2001 and 2002. As discussed in chapter 1, these springtime increases may be linked to increased ammonia availability associated with land management practices particularly on mainland Europe.

There were clear reductions in mass concentrations of ammonium sulphate at both North Kensington and Marylebone Road between 2002 and 2006 and after 2009. With one exception, reductions in concentrations each month were between 10% and more than 50% at both sites. The exception was during January at Marylebone Road where there did not appear to have been any reductions in mass concentrations over the whole period. During the period 2002 to 2006 the mean concentration was 4.3 $\mu g\ m^{-3}$ and it was the same during the period 2009 to 2012.

There were also different seasonal trends between North Kensington and Marylebone Road after 2009. At North Kensington concentrations in the summer months remained high as noted by AQEG (2012) but there was a significant drop in monthly mass concentrations in the summer months at Marylebone Road.

In the next section, the distribution of mass concentrations of ammonium sulphate compared to PM10 mass concentrations is considered to ascertain how, or indeed if, the reductions in ammonium sulphate mass concentrations are more noticeable at different PM mass concentrations.

*Table 4.4* *monthly mean concentrations, ammonium sulphate, Acton Town Hall, 2001 – 2002, North Kensington 2002/2006 and 2009/2012 and Marylebone Road 2002/2006, 2009/2012*

| | Monthly mean concentrations of ammonium sulphate (µg m$^{-3}$) (95%C.I.) | | | | |
|---|---|---|---|---|---|
| | Acton Town Hall | North Kensington | | Marylebone Road | |
| | 2001 - 2002 | 2002 – 2006 | 2009 – 2011 | 2002 – 2006 | 2009 - 2012 |
| **n** | **404** | **1490** | **915** | **1170** | **1013** |
| January | - | 3.8 (3.2,4.2) | 2.9 (2.6,3.5) | 4.3 (3.6,5.1) | 4.2 (3.4,5.3) |
| February | 2.6 (2.3,3.2) | 4.4 (3.7,4.9) | 3.4 (3.0,4.0) | 5.1 (4.4,5.9) | 3.6 (3.1,4.2) |
| March | 4.1 (3.5,4.7) | 4.9 (4.3,5.5) | 3.1 (2.6,3.5) | 5.7 (5.0,6.3) | 3.1 (2.6,3.7) |
| April | 3.8 (3.3,4.3) | 4.9 (4.5,5.5) | 3.5 (3.1,3.9) | 5.0 (4.4,5.5) | 4.6 (3.8,5.4) |
| May | 4.4 (3.6,5.7) | 4.7 (4.3,5.2) | 2.7 (2.5,3.0) | 4.8 (4.4,5.4) | 3.6 (3.2,4.1) |
| June | 4.1 (3.6,4.7) | 4.3 (3.9,4.6) | 3.4 (3.0,3.7) | 4.8 (4.3,5.4) | 3.3 (3.0,3.7) |
| July | 4.2 (3.2,5.2) | 4.4 (3.8,4.9) | 2.9 (2.6,3.2) | 4.7 (4.2,5.3) | 2.6 (2.4,3.0) |
| August | 5.2 (4.2,6.5) | 3.9 (3.5,4.3) | 2.6 (2.3,2.9) | 4.6 (4.1,5.2) | 2.6 (2.3,2.8) |
| September | 4.0 (3.5,4.6) | 4.1 (3.6,4.6) | 3.2 (2.8,3.8) | 4.5 (4.0,5.2) | 2.6 (2.3,3.0) |
| October | 3.2 (2.7,3.7) | 4.1 (3.5,4.7) | 2.5 (2.1,3.1) | 4.4 (3.9,5.0) | 2.4 (2.1,2.8) |
| November | 4.5 (3.7,5.5) | 3.0 (2.7,3.3) | 2.1 (1.7,2.6) | 3.8 (3.4,4.3) | 2.6 (2.2,3.2) |
| December | 6.5 (5.0,7.7) | 4.4 (3.8,5.1) | 2.0 (1.6,2.2) | 4.5 (3.9,5.1) | 2.1 (1.9,2.4) |

*Figure 4.13* *Monthly variation in ammonium sulphate concentrations, Acton Town Hall, 2001 – 2002*

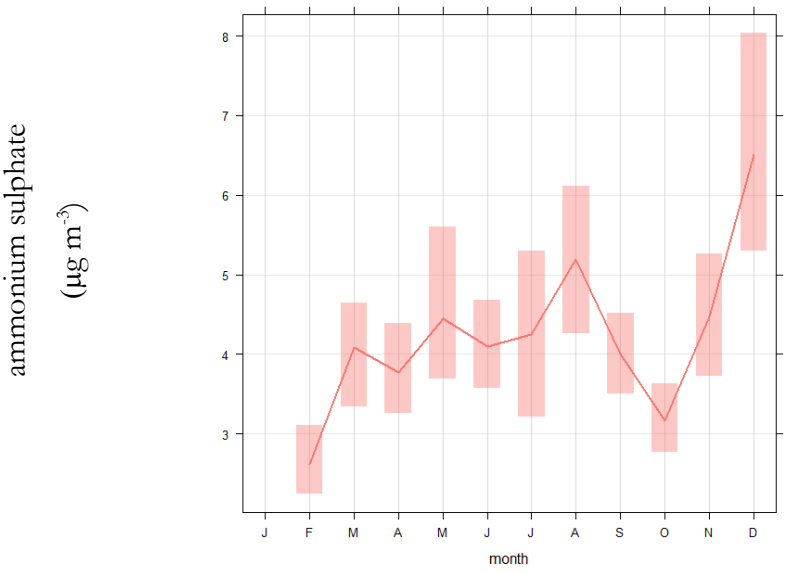


*Figure 4.14 Monthly variation in ammonium sulphate concentrations, Marylebone Road, 2002 - 2006*

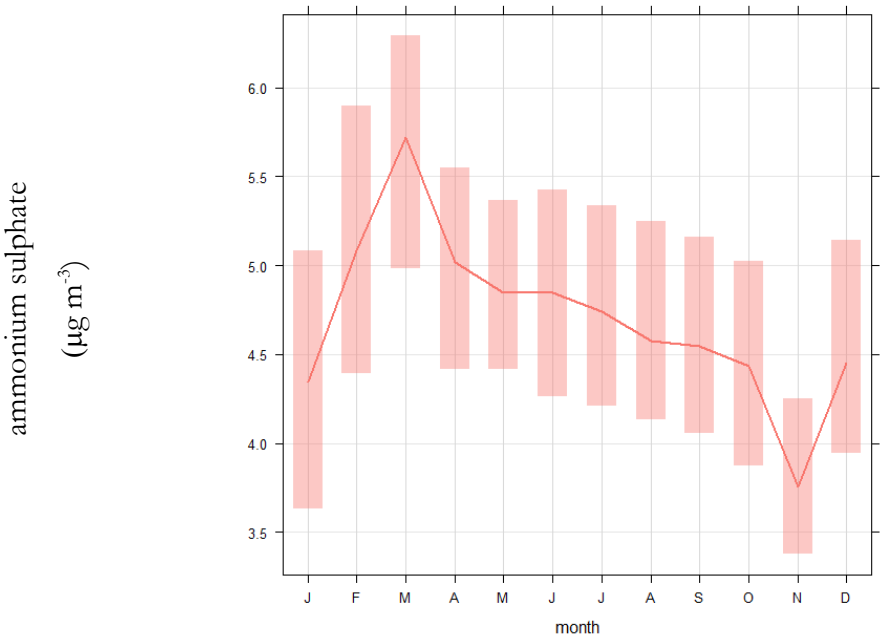
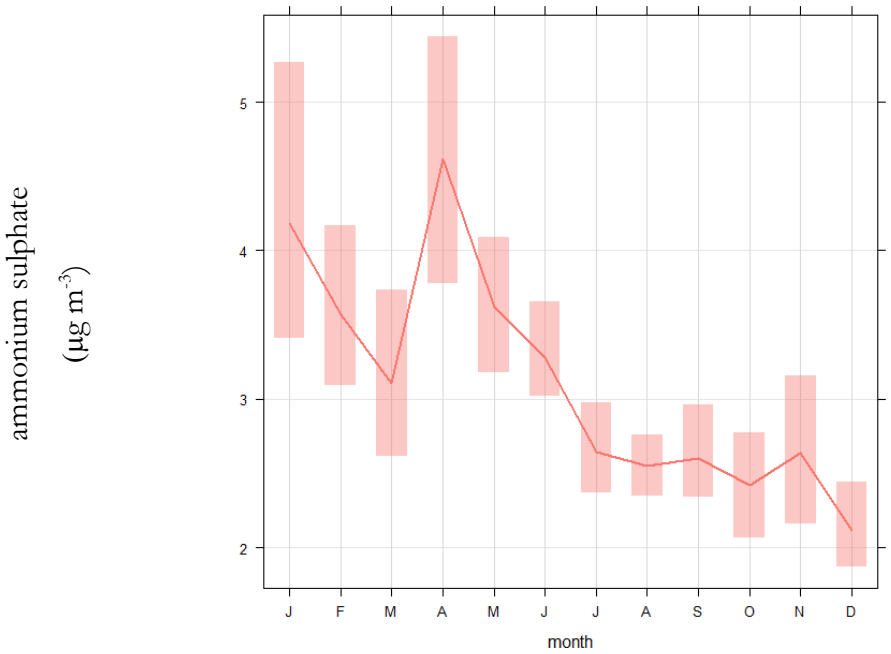



*Figure 4.15 Monthly variation in ammonium sulphate concentrations, Marylebone Road, 2009 – 2012*




N.B. Different y axes

*Figure 4.16 Monthly variation in ammonium sulphate concentrations, North Kensington, 2002 – 2006*

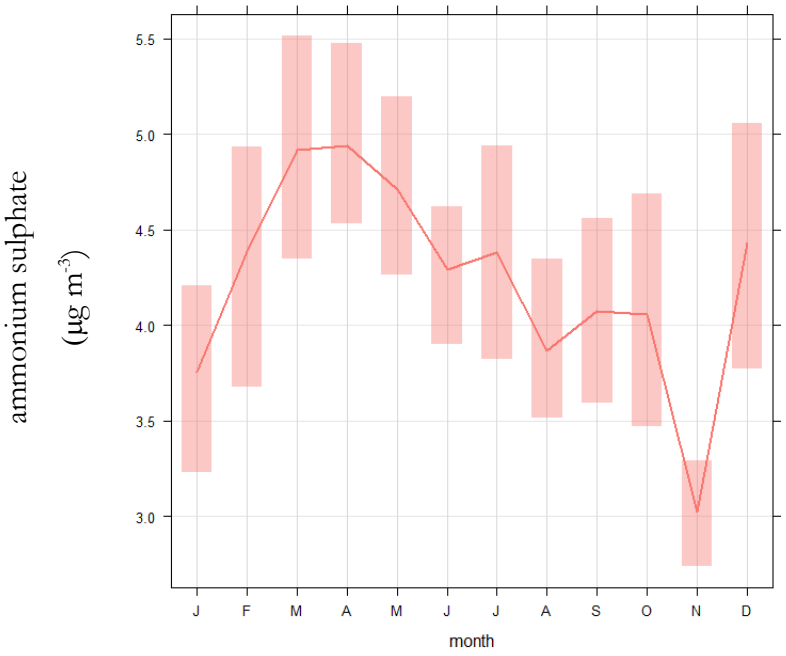
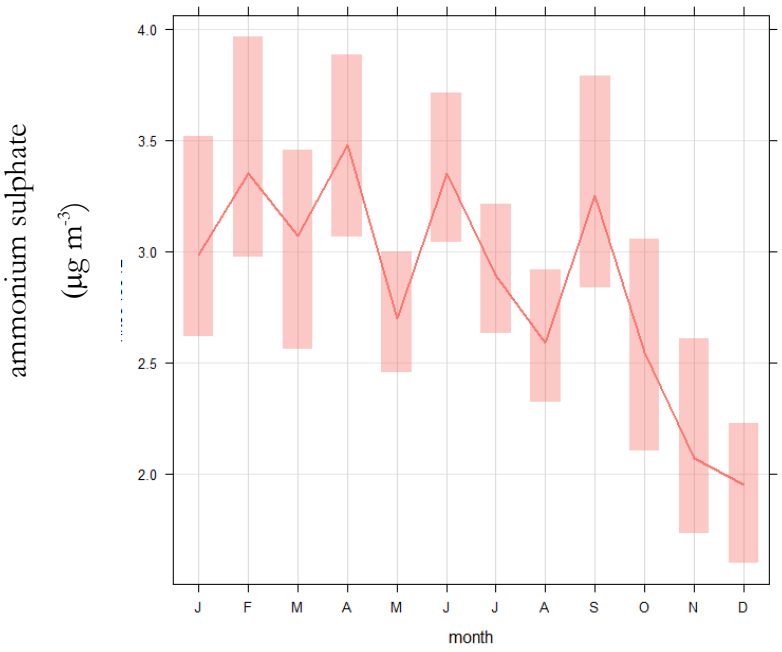



*Figure 4.17 Monthly variation in ammonium sulphate concentrations, North Kensington, 2009 - 2011*




N.B. Different y axes

## *Ammonium sulphate grouped by PM10 concentrations*

Mean ammonium sulphate mass concentrations have been calculated for each PM10 mass concentration 'bin'. In order to provide a useful comparison, as in chapter 3, only those days at Marylebone Road and North Kensington where measurements of both the PM mass concentration and anions have been used for this analysis (n = 737 for 2002 – 2006 and n = 523 for 2009 onwards). Details of the analysis are set out in Table 4.5.

At Acton Town Hall mass concentrations of ammonium sulphate increased from a mean concentration of 3.2 μg $m^{-3}$ when mean PM10 concentrations were less than 30 μg $m^{-3}$ (i.e. the majority of the sampling days) to a mean concentration of 11.6 μg $m^{-3}$ on days when the daily limit value was exceeded. However the percentage contribution was largely unchanged at 13 to 16%. A similar pattern was observable at North Kensington between 2002 and 2006 and the mean PM10 mass concentration on the majority of sample days was also the same. At Marylebone Road the majority of days occurred when mean PM10 concentrations were in the 30 – 50 μg $m^{-3}$ mean concentration 'bins'. The percentage contribution remained constant at each concentration 'bin' at approximately 11% which is slightly less than the contribution made towards mean PM10 concentrations at Acton Town Hall and North Kensington. Yin and Harrison (2008) in a study in Birmingham, UK between 2004 and 2006 and reported in relation to PM2.5, by AQEG (2012) found that ammonium sulphate (corrected for particle bound water by increasing by a factor of 1.29) contributed 18.2% to overall PM10 mass on days when the daily limit value was exceeded compared to 16% on all days: not dissimilar to this study for the same period.

After 2009, as reported in chapter 3, PM10 sampling at North Kensington and Marylebone Road was carried out using a different filter substrate (Emfab™) and it was noted that PM10 mass concentrations were generally lower at both sites. On the majority of sample days at North Kensington mean PM10 mass concentrations were lower than 20 μg $m^{-3}$ and mean ammonium sulphate concentrations contributed in the region of 20% to mean PM10 mass concentrations. By contrast, at Marylebone Road the majority of days were at a PM10 mass concentration of 40 μg $m^{-3}$ or less and ammonium sulphate concentrations were similar to those measured at North Kensington but contributed approximately 8% to total PM10 mass concentrations. On days when the daily limit value was exceeded ammonium sulphate

contributed approximately 11% to overall PM mass concentrations, i.e. less than on days when the daily limit value was not exceeded. This represents a change in apparent pollutant behaviour with sulphate making a diminished contribution to days when the daily limit value was exceeded in the post 2009 Emfab™ dataset.

*Table 4.5 mean concentrations of ammonium sulphate grouped by PM10 concentration 'bin'*

*,*

| | **PM10 concentration 'bin'** | | | | | |
|---|---|---|---|---|---|---|
| **Site Sampling period** | **<20 (95% C.I)** | **20 – 30 (95% C.I)** | **30 – 40 (95%C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95%C.I.)** | **>60 (95% C.I.)** |
| | **ammonium sulphate (µg m$^{-3}$)** | | | | | |
| | Quartz fibre filters | | | | | |
| Acton Town Hall 2001 – 2002 | 2.2 (2.1,2.4) | 3.2 (3.0,3.4) | 4.6 (4.2,4.9) | 6.4 (5.6,7.1) | 7.6 (6.6,8.6) | 11.6 (8.6,14.5) |
| %age contribution to PM10 concentration | 14% | 13% | 13% | 14% | 14% | 16% |
| No of sample days | 81 | 154 | 91 | 35 | 30 | 13 |
| North Kensington 2002 - 2006 | 2.2 (2.1,2.4) | 3.4 (3.2,3.6) | 5.4 (5.0,5.8) | 7.2 (6.5,7.9) | 8.5 (7.4,9.6) | 11.3 (9.3,13.4) |
| %age contribution to PM10 concentration | 14% | 14% | 16% | 16% | 16% | 16% |
| No of sample days | 192 | 301 | 143 | 59 | 19 | 23 |
| Marylebone Road 2002 - 2006 | 1.9 (1.5,2.4) | 3.1 (2.8,3.3) | 3.6 (3.3,3.9) | 4.4 (4.1,4.7) | 6.0 (5.4,6.5) | 8.2 (7.3,9.1) |
| %age contribution to PM10 concentration | 12% | 12% | 10% | 10% | 11% | 11% |
| No of sample days | 21 | 113 | 218 | 188 | 108 | 89 |
| | Emfab™ filters | | | | | |
| North Kensington 2009 - 2011 | 2.4 (2.2,2.5) | 3.2 (2.8,3.6) | 4.1 (3.3,4.8) | 5.9 (4.9,7.0) | 6.5 (5.3,7.6) | |
| %age contribution to PM10 concentration | 20% | 14% | 12% | 13% | 11% | - |
| No of sample days | 374 | 88 | 32 | 20 | 9 | - |
| Marylebone Road 2009 - 2011 | 2.4 (2.1,2.6) | 2.3 (2.1,2.5) | 2.6 (2.4,2.9) | 3.4 (2.9,3.9) | 5.1 (3.4,6.9) | 7.6 (5.4,9.8) |
| %age contribution to PM10 concentration | 15% | 9% | 8% | 8% | 9% | 11% |
| No of sample days | 82 | 135 | 167 | 86 | 28 | 25 |

Comparing concentrations at each site on the same day may provide some information about whether a roadside enhancement of ammonium sulphate at Marylebone Road is discernible. Mean ammonium sulphate concentrations at both sites have therefore been grouped according to PM10 concentrations at Marylebone Road for both time periods. Details are set out in Table 4.6 below and illustrated in Figures 4.18 and 4.19.

Between 2002 and 2006 ammonium sulphate concentrations seem to increase similarly at both sites. It is difficult to compare directly with concentrations in the same PM10 mass concentration 'bins' after 2009 because of the filter substrate change. After 2009, at lower PM10 mass concentrations ammonium sulphate mean concentrations remain similar between the two sites but on days when the daily limit value was exceeded at Marylebone Road ammonium sulphate concentrations were in the region of 50% higher (+2.5 μg $m^{-3}$). The roadside increment also increases with increasing ammonium sulphate concentrations suggesting different local sources. There is therefore some evidence that there is a roadside contribution to ammonium sulphate concentrations on days when the daily limit value is exceeded, particularly after 2009. Jones and Harrison (2011) noted that the Environment Agency had recorded higher concentrations of sulphur dioxide, a precursor species for sulphate, at Marylebone Road compared to the top of the nearby BT Tower and considered that this indicated 'a continued ground-level source' from road traffic because there had been insufficient time for sulphate to form.

*Table 4.6* *Same day mean ammonium sulphate concentrations, Marylebone Road and North Kensington, based on PM10 mean concentration 'bins' at Marylebone Road*

| | **PM10 concentration 'bin' at Marylebone Road** | | | | | |
|---|---|---|---|---|---|---|
| **Site** | **<20 (95% C.I)** | **20 – 30 (95% C.I)** | **30 – 40 (95%C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95%C.I.)** | **>60 (95% C.I.)** |
| | **ammonium sulphate(μg $m^{-3}$)** | | | | | |
| | **2002 – 2006** | | | | | |
| No of sample days | 21 | 113 | 218 | 188 | 108 | 89 |
| Marylebone Road | 1.9 (1.5,2.4) | 3.1 (2.8,3.3) | 3.6 (3.3,3.9) | 4.4 (4.1,4.7) | 6.0 (5.4,6.5) | 8.2 (7.3,9.1) |
| North Kensington | 1.8 (1.4,2.3) | 2.9 (2.6,3.2) | 3.2 (2.9,3.4) | 4.0 (3.6,4.3) | 5.4 (4.8,5.9) | 7.8 (6.9,8.7) |
| | **2009 – 2011** | | | | | |
| No of sample days | 82 | 135 | 167 | 86 | 28 | 25 |
| Marylebone Road | 2.4 (2.1,2.6) | 2.3 (2.1,2.5) | 2.6 (2.4,2.9) | 3.4 (2.9,3.9) | 5.1 (3.4,6.9) | 7.6 (5.4,9.8) |
| North Kensington | 2.8 (2.5,3.1) | 2.3 (2.1,2.6) | 2.5 (2.3,2.8) | 3.0 (2.7,3.4) | 4.2 (3.2,5.3) | 5.1 (4.2,6.0) |

Figure 4.18 *Same day mean ammonium sulphate concentrations, Marylebone Road and North Kensington, based on mean PM10 concentration 'bins' at Marylebone Road, 2002 – 2006*

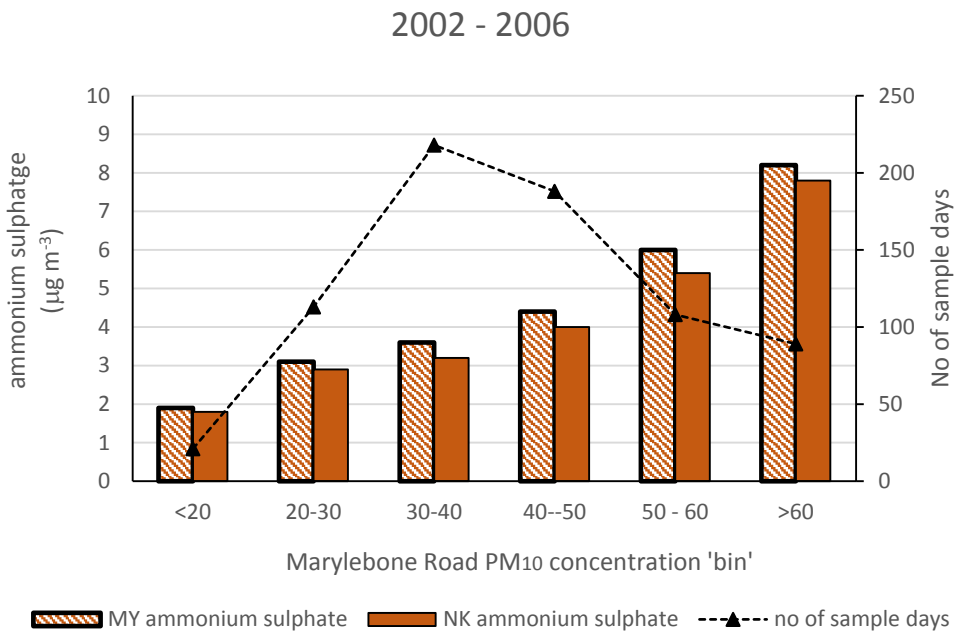
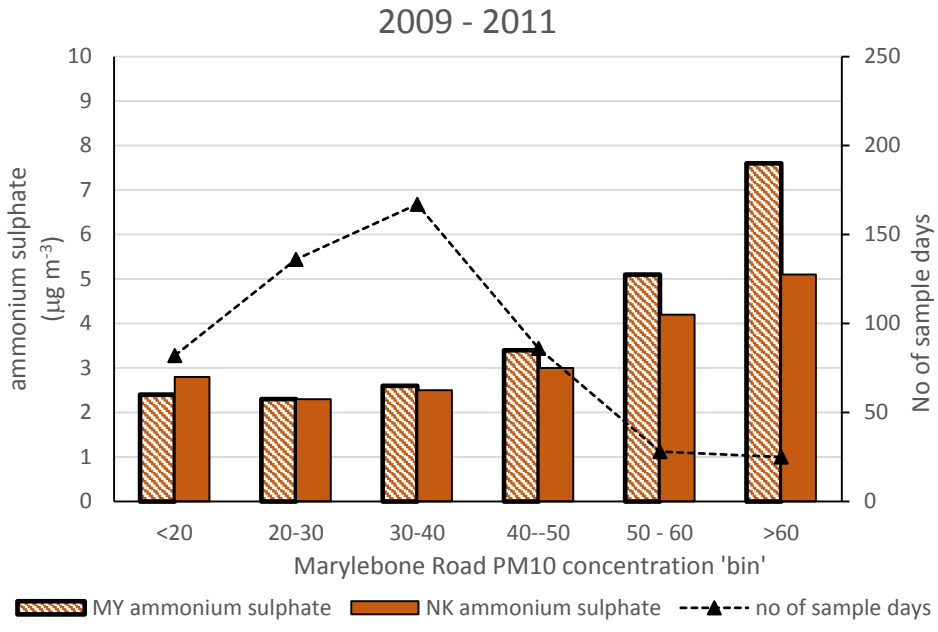



Figure 4.19 *Same day mean ammonium sulphate concentrations, Marylebone Road and North Kensington, based on mean PM10 concentration 'bins' at Marylebone Road, 2009 – 2011*



# AMMONIUM NITRATE

Figures 4.20 – 4.22 are the time series graphs illustrating ammonium nitrate concentrations at each site (Acton Town Hall, North Kensington and Marylebone Road). On occasions, particularly at Acton Town Hall, the amount of ammonium nitrate recorded was zero. It is unlikely that there was no contribution to PM10 concentrations by ammonium nitrate on those occasions but due to the volatility of the species it may have been below the detection limits of ion chromatography.

Figure 4.23 illustrates by way of boxplots the distribution of measurements at each site. It would seem from the time series plots that, not only was there daily variation in ammonium nitrate concentrations, but there also appeared to be different concentrations at the different sites with the highest concentrations recorded at Marylebone Road. However as may be seen from the boxplots in Figure 4.23 and Table 4.7 mean concentrations (arithmetic) were very similar at all three sites (4.5 – 5.2 $\mu g\ m^{-3}$) and it is the maxima recorded at each site that were different.

Unlike ammonium sulphate, no step change in mass concentrations during 2008 was noticeable which also provides confidence that the change in sulphate concentrations was not a problem with the IC analysis method.

The maximum ammonium nitrate concentration at Marylebone Road was 65.0 μg $m^{-3}$ on 23 March 2012. The PM10 concentration on that day was 80 μg $m^{-3}$. Ammonium nitrate therefore comprised in the region of 80% of the PM10 concentration on that date. As may be seen in Table 3.4 in chapter 3, 23 March 2012 was also identified as a high PM10 concentration date at North Kensington and Oxford Street. No anion analysis has been reported in respect of that date at North Kensington but it would seem likely that ammonium nitrate concentrations would also have been high and making a significant contribution to PM10 concentrations. There would also appear to be a roadside increment at Marylebone Road in the region of 0.7 μg $m^{-3}$ when compared with North Kensington, suggesting local formation of ammonium nitrate as suggested by Kleeman et al. (2005).

*Table 4.7 mean and maximum concentrations of ammonium nitrate at the study sites*

| **Site** | **Sampling period** | **No of sample days** | **Mean (95%C.I.)** | **Maximum (date)** |
|---|---|---|---|---|
| | | | ammonium nitrate (μg $m^{-3}$) | |
| Acton Town Hall | January 2001 – December 2002 | 404 | 4.5 (4.1,4.9) | 23.1 (8.5.02) |
| North Kensington | 2002 – 2011 | 3114 | 4.5 (4.4,4.7) | 39.9 (2.4.05) |
| Marylebone Road | 2002 - 2012 | 2825 | 5.2 (5.0,5.4) | 65.0 (23.3.12) |

It appears from Figure 4.21 that maximum concentrations at Marylebone Road in particular have increased over time, especially during the spring months.

*Figure 4.20 time series of ammonium nitrate concentrations, Acton Town Hall 2001 - 2002*

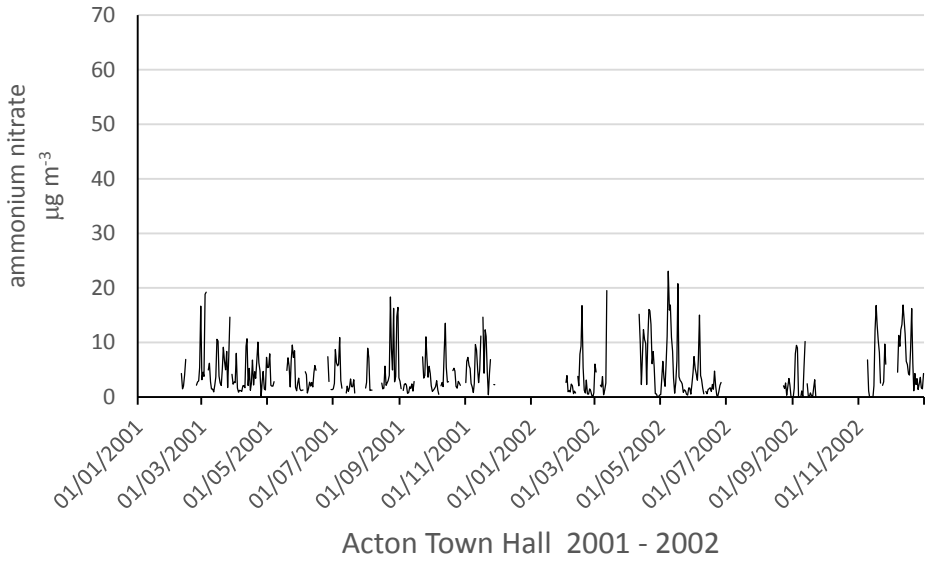



*Figure 4.21 time series of ammonium nitrate concentrations, Marylebone Road, 2002 - 2012*

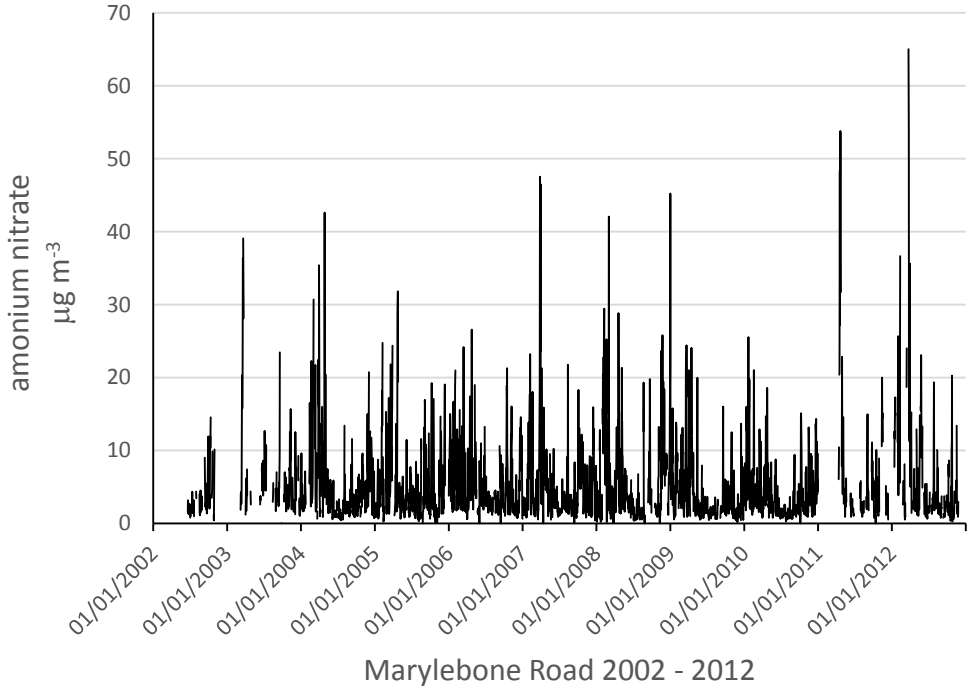


*Figure 4.22 time series of ammonium nitrate concentrations, North Kensington, 2002 - 2011*

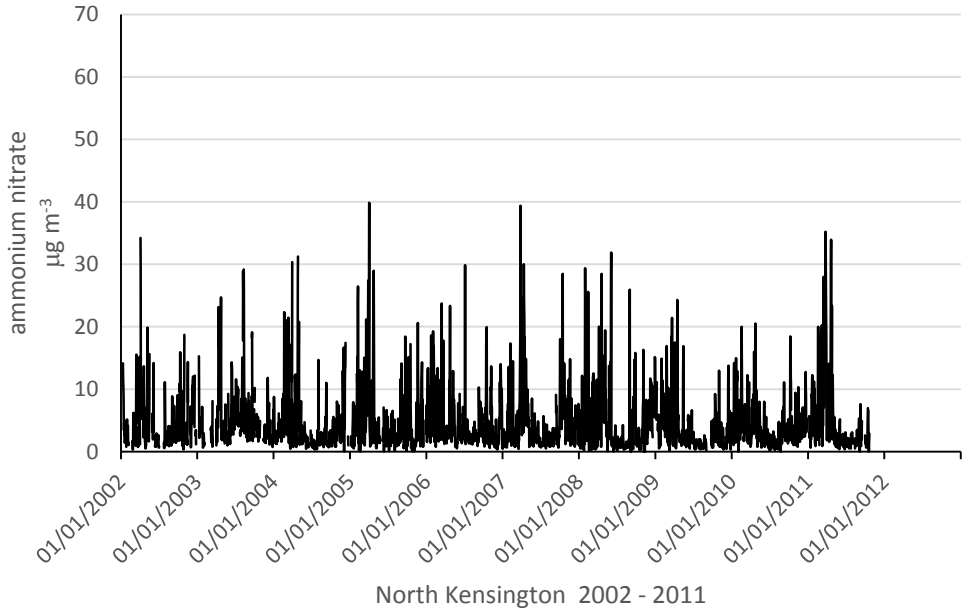
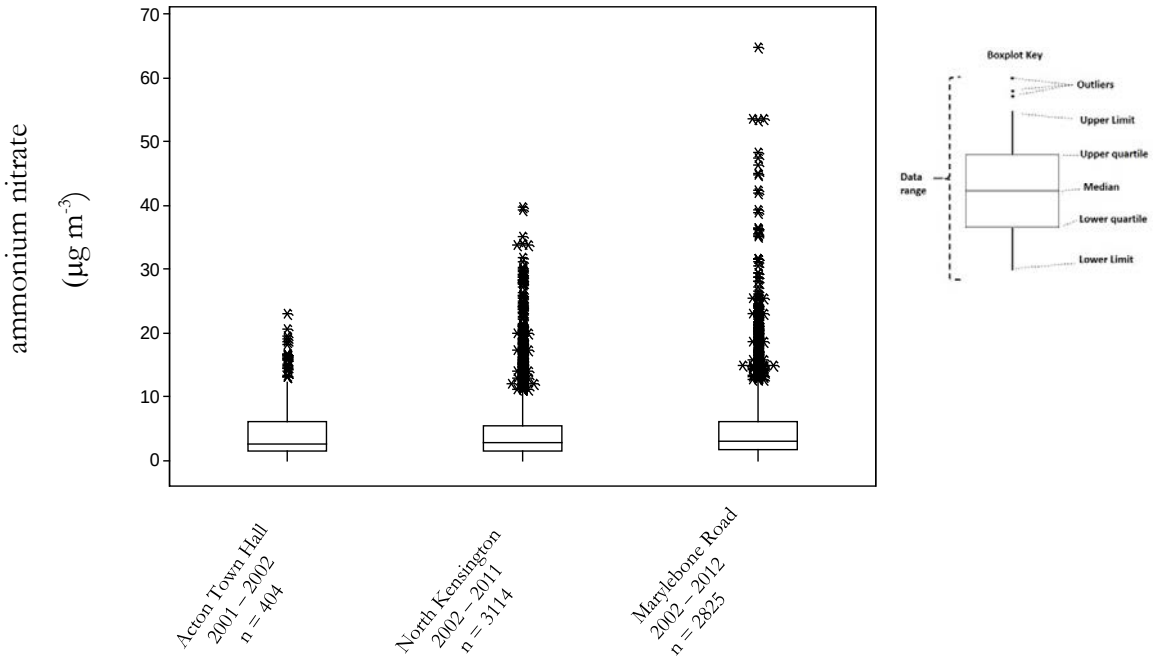



*Figure 4.23 Boxplots comparing concentrations of ammonium nitrate, Acton Town Hall, 2001 – 2002, North Kensington 2002 – 2011, Marylebone Road 2002 – 2012*



## Trend Analysis (ammonium nitrate)

Trend analysis using the TheilSen function in Openair (Carslaw and Ropkins, 2012) was carried out and is reported in Figures 4.24 to 4.26 and Table 4.8. There was a small decreasing trend at each site but it was not significant at either Acton Town Hall or Marylebone Road. A small downward trend was significant at p <0.05 at North Kensington, contrasting with ammonium sulphate which showed a significant trend between 2002 and 2012 at Marylebone Road and North Kensington.

*Table 4.8 Summary of TheilSen trend analysis and statistical significance, ammonium nitrate*

| Ammonium nitrate | | | | |
|---|---|---|---|---|
| **Site** | **Sampling period** | **No of sample days** | **trend (µg $m^{-3}$) per year (95% C.I.)** | **p** |
| Acton Town Hall | 2001 – 2002 | 404 | -0.26 (-1.62, 1.61) | >0.1 |
| North Kensington | 2002 - 2011 | 3114 | -0.10 (-0.17,-0.01) | <0.05 |
| Marylebone Road | 2002 - 2012 | 2825 | -0.11 (-0.25, 0.03) | >0.1 |

*Figure 4.24* *TheilSen analysis, ammonium nitrate, Acton Town Hall 2001 – 2002 (p = >0.1)*

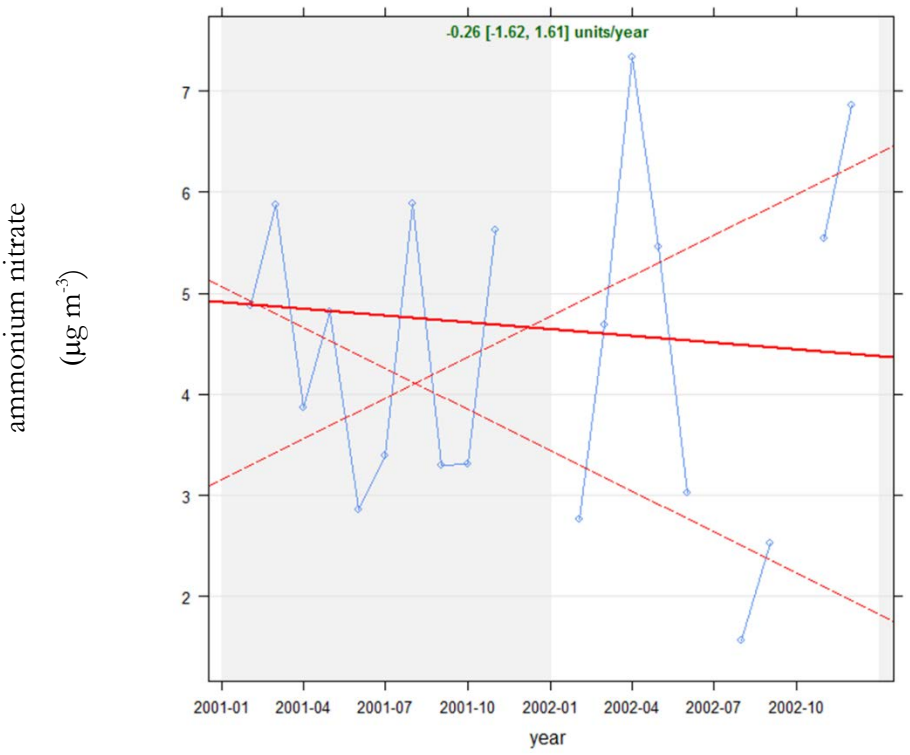


*Figure 4.25* *TheilSen analysis, ammonium nitrate, Marylebone Road 2002 – 2012 (p = >0.1)*

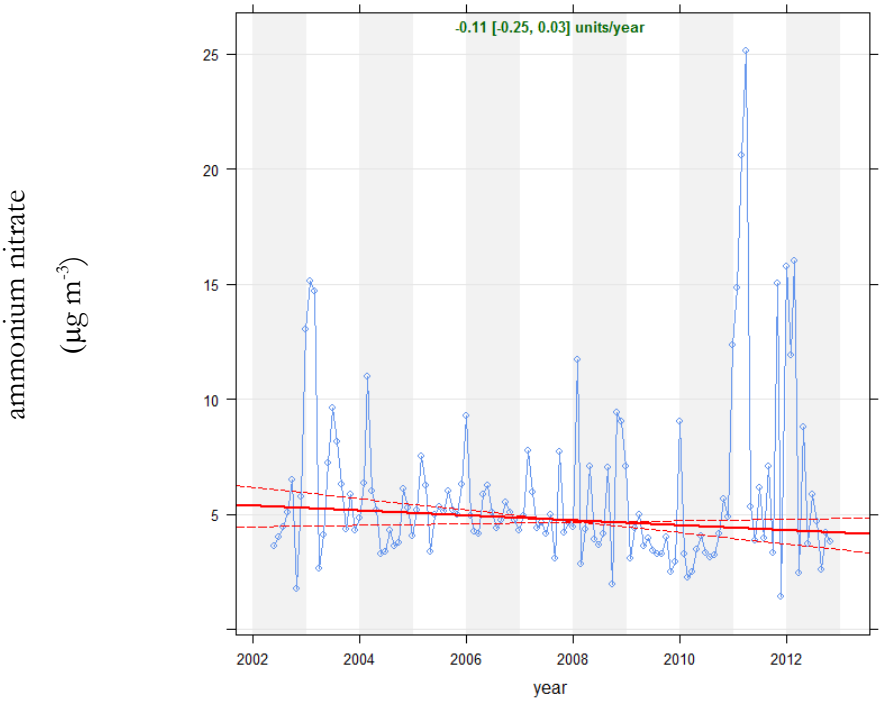
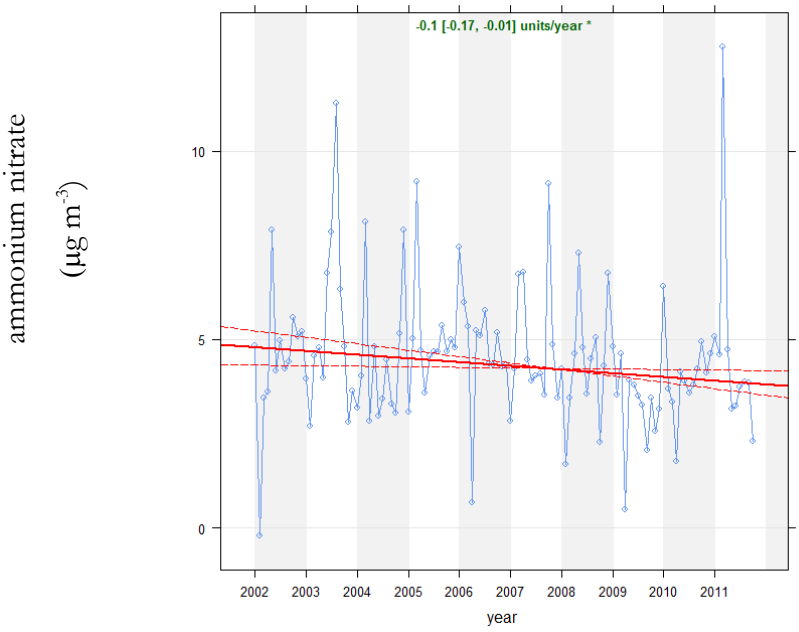



*Figure 4.26* *TheilSen analysis, ammonium nitrate, North Kensington, 2002 – 2011 (p = <0.05)*



## *Day of the week and Monthly Trends (ammonium nitrate)*

As may be observed in Figures 4.27 – 4.28 the lowest daily mean concentration of ammonium nitrate at each sampling location occurred on a Sunday but there were no distinctive daily differences identifiable when taking into account the uncertainty identified by the 95% confidence intervals (illustrated by the pink rectangles). At Acton Town Hall the highest mean concentration occurred on Thursdays (5.3 μg $m^{-3}$) with a mean concentration of4.1 μg $m^{-3}$ on Sundays. At Marylebone Road the maximum daily concentration of 5.6 μg $m^{-3}$ occurred midweek on Wednesdays and the mean concentration on Sundays was 4.1 μg $m^{-3}$. North Kensington had the highest mean concentration on a different day to both Marylebone Road and Acton Town Hall. At that location it occurred on Thursdays (5.3 μg $m^{-3}$) but the mean concentration on Sundays was the same as Marylebone Road (4.1 μg $m^{-3}$).

The formation of particulate nitrate is linked to NOx emissions which are a product of combustion and an indicator of local traffic sources. Kleeman et al. (2005) found that approximately 50% of ammonium nitrate was from local sources in their study in California, US. If local sources of ammonium nitrate were making a similar contribution at the study sites in this project then it might be expected that there would be greater detectable differences in concentrations at weekends (perhaps more in line with the PM mass concentrations reported in chapter 3). However, it is possible that the lower levels observed on Sundays may have been linked to local emissions.

*Figure 4.27 day of the week variation in ammonium nitrate concentrations, Acton Town Hall, 2001 - 2002*

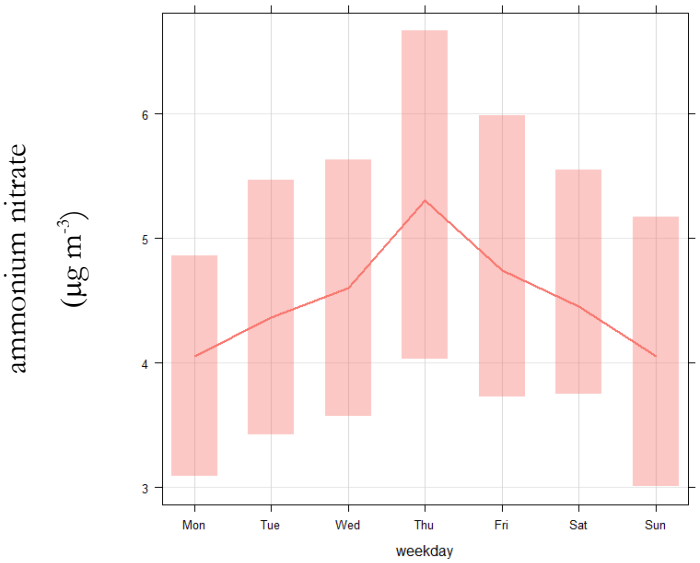
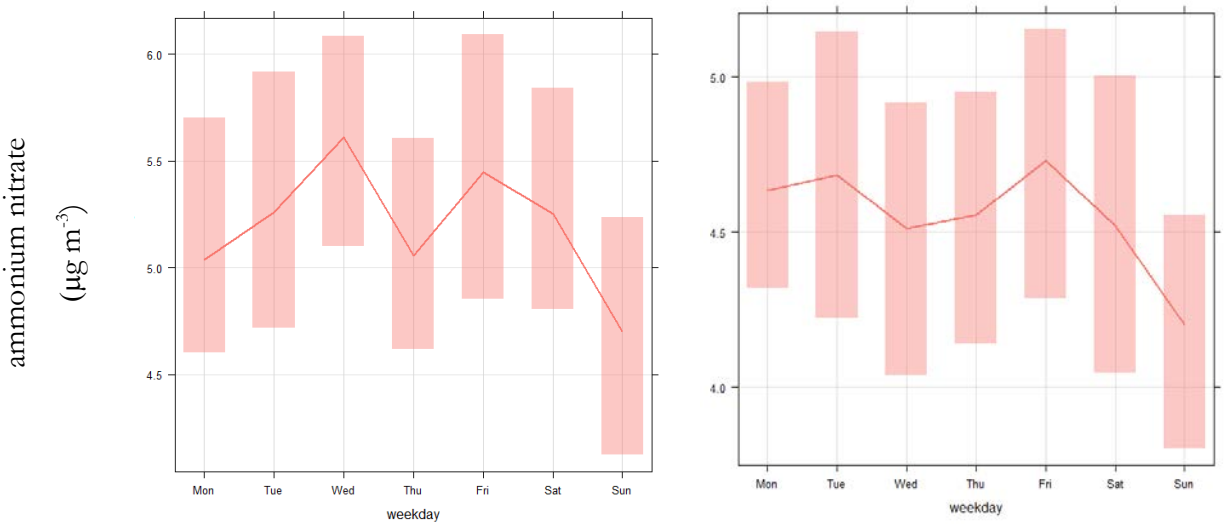



*Figure 4.28 day of the week variation in ammonium nitrate concentrations, (a) Marylebone Road 2002 – 2012 and (b) North Kensington 2002 - 2011*

(a) (b)



Figures 4.29 to 4.31 show the monthly variations in ammonium nitrate concentrations at each site.

At both Marylebone Road and North Kensington there were clear seasonal differences in ammonium nitrate concentrations with lowest mean concentrations being recorded in July (mean 2.5 μg $m^{-3}$ and 2.3 μg $m^{-3}$ respectively) at each site. Mean concentrations steadily increased and at both sites reached maximum mean concentrations in April (mean 9.0 μg $m^{-3}$ and 8.2 μg $m^{-3}$ respectively). Greater losses of ammonium nitrate from filter samples due to volatilisation would occur in the warmer months however this behaviour contrasts with the higher mean concentrations in April when compared to the colder conditions in, say, December or January when mean concentrations were lower in the region of 4.0 μg $m^{-3}$ and 5.0 μg $m^{-3}$ respectively at each location. There would seem to be at least a doubling of concentrations in the spring months when compared to the summer months. A similar pattern is reported by AQEG (2012) and Harrison et al. (2012) and was attributed to regional sources affecting concentrations. It is probable that increased ammonia concentrations in the spring months from land management practices on continental Europe, in particular the Netherlands and Belgium, discussed in chapter 1 are an important factor. Harrison and Yin (2010) however found no seasonal differences in nitrate concentrations at two sites in Birmingham between May 2007 and April 2008.

The seasonal behaviour at Acton Town Hall is different to the patterns observed at both Marylebone Road and North Kensington which was probably due to gaps in the dataset. Nevertheless, lower mean concentrations were recorded in the summer months (June and July) and the maximum mean concentration was recorded in December, suggesting that there were seasonal differences at that location.

*Figure 4.29 monthly variation in ammonium nitrate concentrations, Acton Town Hall, 2001 - 2002*

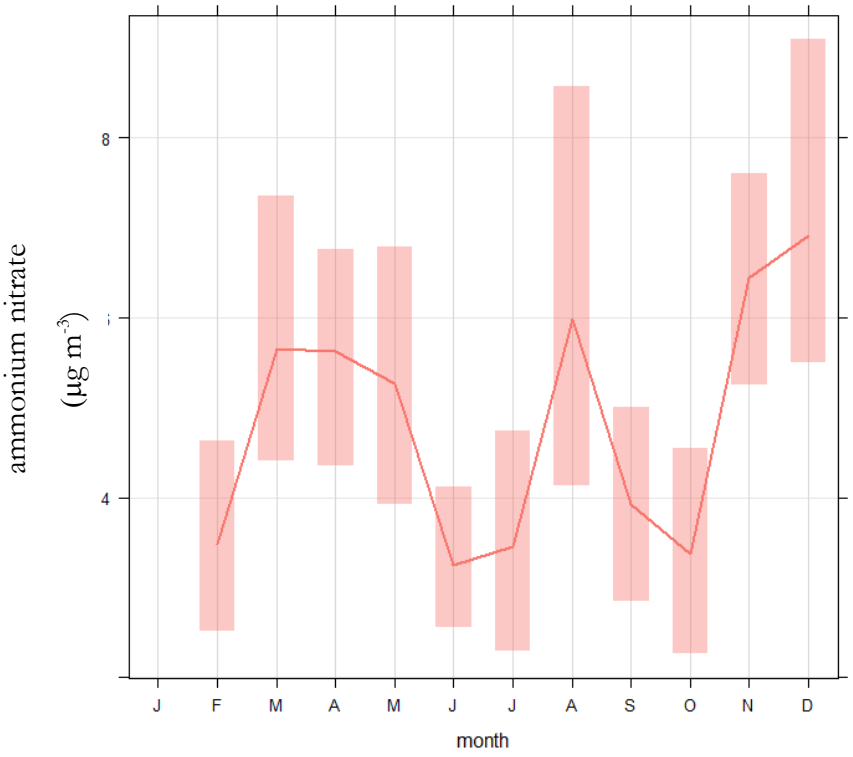


*Figure 4.30* *monthly variation in ammonium nitrate concentrations, Marylebone Road 2002 - 2012*

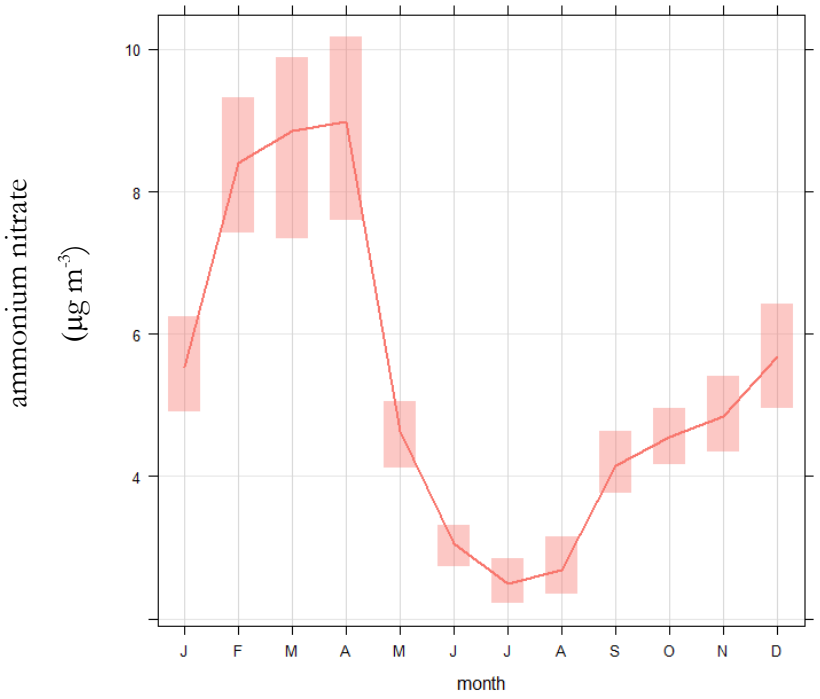
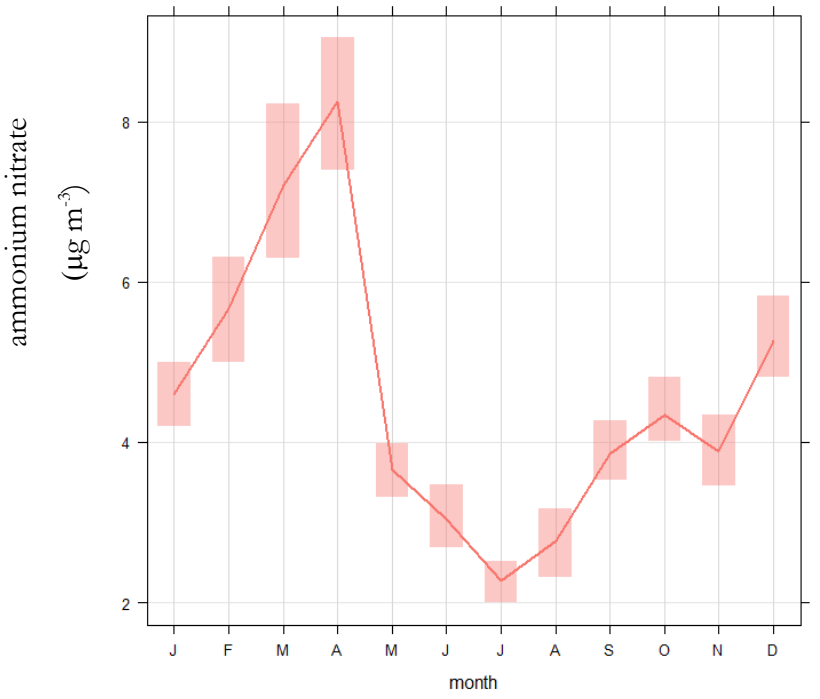



*Figure 4.31* *monthly variation in ammonium nitrate concentrations, North Kensington 2002 - 2011*



## *Ammonium nitrate grouped by PM10 concentrations*

Table 4.9 sets out the mean concentrations of ammonium nitrate grouped by PM10 concentration 'bin'. At Acton Town Hall on the majority of days (<PM10 30 μg $m^{-3}$) mean ammonium nitrate concentrations were below 2.6 μg $m^{-3}$ and contributed 11 % to PM10 mass concentrations. However when the daily limit value was exceeded (n= 43) mean ammonium nitrate concentrations contributed approximately 20% to mean PM10 mass concentrations. This pattern was repeated at North Kensington between 2002 and 2006, with a doubling of the percentage contribution made by the ammonium nitrate species on high pollution days. Similar doubling of percentage values for ammonium nitrate were reported by Yin and Harrison (2008) and AQEG (2012). This percentage increase was not as noticeable at Marylebone Road for the same time period due to greater primary PM at this site. On days when the daily limit value was not exceeded mean ammonium nitrate concentrations contributed approximately 11% to overall PM10 mass concentrations and this rose to 17% on high pollution days. Similarly, the percentage contribution during the period 2009 to 2011 made by mean ammonium nitrate concentrations doubled when comparing the days when the daily limit value was not exceeded to other days.

In contrast to ammonium sulphate, it would seem that ammonium nitrate concentrations were influential on increasing PM10 mass concentrations, particularly on days when the daily limit value was exceeded and there has been no real change in this behaviour during the last decade.

*Table 4 9 mean concentrations of ammonium nitrate grouped by PM10 concentration 'bin'*

| | **PM10 concentration 'bin'** | | | | | |
|---|---|---|---|---|---|---|
| **Site Sampling period** | **<20 (95% C.I)** | **20 – 30 (95% C.I)** | **30 – 40 (95%C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95%C.I.)** | **>60 (95% C.I.)** |
| | **ammonium nitrate (μg $m^{-3}$)** | | | | | |
| | Quartz fibre filters | | | | | |
| Acton Town Hall 2001 – 2002 | 1.4 (1.2,1.6) | 2.6 (2.3,2.8) | 5.2 (4.5,5.9) | 8.4 (7.1,9.7) | 11.8 (10.2,13.5) | 14.3 (11.4,17.2) |
| %age contribution to PM10 concentration | 9% | 11% | 15% | 19% | 22% | 19% |
| No of sample days | 81 | 154 | 91 | 35 | 30 | 13 |
| North Kensington 2002 - 2006 | 2.0 (1.8,2.2) | 3.5 (3.1,3.7) | 5.4 (4.9,5.9) | 9.4 (7.8,10.8) | 11.0 (8.8,13.3) | 17.8 (14.4,21.1) |
| %age contribution to PM10 concentration | 13% | 14% | 16% | 21% | 20% | 25% |
| No of sample days | 192 | 301 | 143 | 59 | 19 | 23 |
| Marylebone Road 2002 - 2006 | 1.9 (1.4,2.4) | 2.7 (2.3,3.0) | 3.7 (3.3,4.0) | 4.4 (3.9,4.8) | 6.8 (6.0,7.7) | 12.4 (10.7,14.1) |
| %age contribution to PM10 concentration | 12% | 11% | 11% | 10% | 13% | 17% |
| No of sample days | 21 | 113 | 218 | 188 | 108 | 89 |
| | Emfab™ filters | | | | | |
| North Kensington 2009 - 2011 | 2.3 (2.2,2.5) | 4.9 (4.4,5.4) | 7.8 (6.3,9.3) | 13.2 (11.4,15.0) | 21.4 (16.2,26.6) | - |
| %age contribution to PM10 concentration | 19% | 22% | 23% | 30% | 38% | - |
| No of sample days | 374 | 88 | 32 | 20 | 9 | - |
| Marylebone Road 2009 - 2011 | 2.3 (2.0,2.6) | 2.8 (2.4,3.1) | 3.4 (2.9,3.8) | 6.0 (5.0,7.0) | 9.4 (6.6,12.2) | 20.6 (14.2,27.0) |
| %age contribution to PM10 concentration | 15% | 11% | 10% | 14% | 17% | 30% |
| No of sample days | 82 | 135 | 167 | 86 | 28 | 25 |

As with ammonium sulphate, ammonium nitrate mean concentrations have also been compared between North Kensington and Marylebone Road on the same day grouped according to PM10 concentration 'bin' at Marylebone Road. The results are set out in Table 4.10 and illustrated in Figures 4.32 and 4.33.

During 2002 to 2006 mean ammonium nitrate concentrations were similar at each PM10 concentration 'bin' even on days when the daily limit value was exceeded suggesting that there was no roadside enhancement at Marylebone Road during that period. During 2009 to 2011 concentrations remain similar on days when the daily limit value is not exceeded but on high pollution days mean concentrations were higher at Marylebone Road. It would seem there may have been a roadside enhancement at Marylebone Road after 2009 indicating that local sources have become more important. However it should be noted that there was no reduction in ammonium nitrate concentrations here in line with the trend analysis reported above.

When PM10 concentrations were below 50 μg $m^{-3}$ ammonium nitrate and ammonium sulphate (reported above) mean concentrations were similar during both time periods at each concentration 'bin'. However on days when the daily limit value was exceeded ammonium nitrate was much more influential on PM10 mass concentrations than ammonium sulphate.

*Table 4.10 mean concentrations of ammonium nitrate grouped by PM10 concentration 'bin"*

| | **PM10 concentration 'bin' at Marylebone Road** | | | | | |
|---|---|---|---|---|---|---|
| **Site** | **<20 (95% C.I)** | **20 – 30 (95% C.I)** | **30 – 40 (95%C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95%C.I.)** | **>60 (95% C.I.)** |
| | **ammonium nitrate (μg $m^{-3}$)** | | | | | |
| | **2002 - 2006** | | | | | |
| No of sample days | 21 | 113 | 218 | 188 | 108 | 89 |
| Marylebone Road | 1.9 (1.4,2.4) | 2.7 (2.3,3.0) | 3.7 (3.3,4.0) | 4.4 (3.9,4.8) | 6.8 (6.0,7.7) | 12.4 (10.7,14.1) |
| North Kensington | 1.8 (1.4,2.3) | 2.3 (2.0,2.6) | 3.2 (2.9,3.5) | 3.8 (3.4,4.2) | 6.2 (5.4.7.1) | 11.1 (9.5,12.6) |
| | **2009 - 2011** | | | | | |
| No of sample days | 82 | 135 | 167 | 86 | 28 | 25 |
| Marylebone Road | 2.3 (2.0,2.6) | 2.8 (2.4,3.1) | 3.4 (2.9,3.8) | 6.0 (5.0,7.0) | 9.4 (6.6,12.2) | 20.6 (14.2,27.0) |
| North Kensington | 2.5 (2.2,2.8) | 2.5 (2.2,2.9) | 2.9 (2.6,3.3) | 4.8 (4.1,5.5) | 7.9 (5.7,10.1) | 14.3 (11.1,17.6) |

*Figure 4.32* *Same day mean ammonium nitrate concentrations, Marylebone Road and North Kensington, based on mean PM10 concentrations 'bins' at Marylebone Road 2002 - 2006*

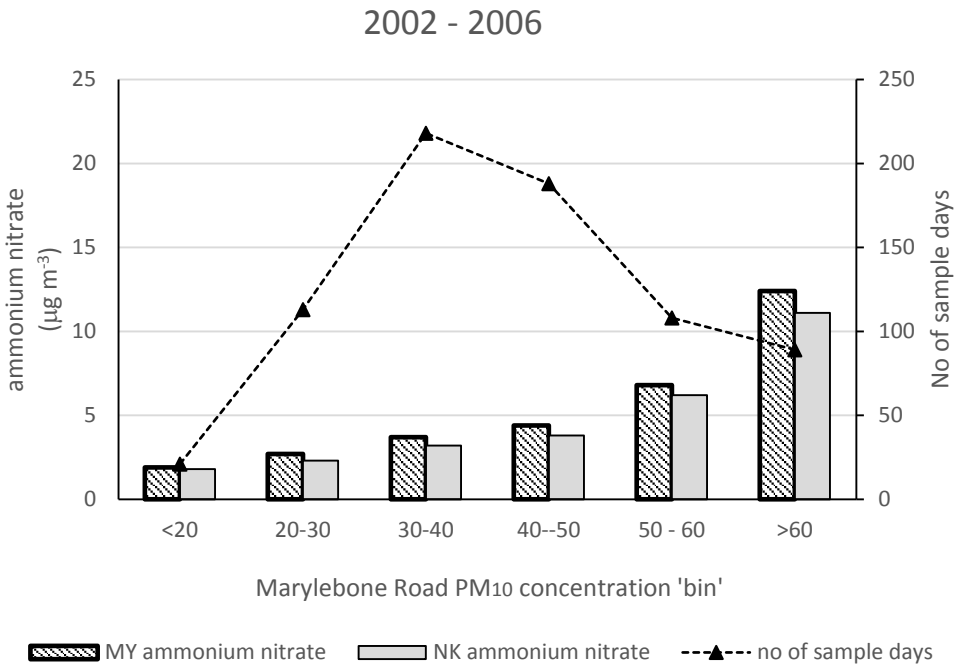
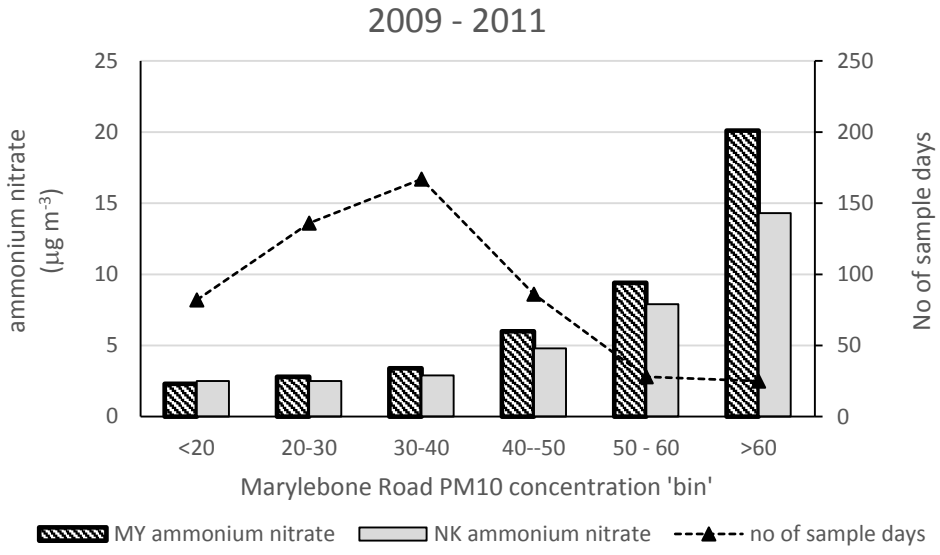



*Figure 4.33* *Same day mean ammonium nitrate concentrations, Marylebone Road and North Kensington, based on mean PM10 concentrations 'bins' at Marylebone Road 2009 - 2011*



## *Comparison of ammonium nitrate and sodium nitrate concentrations at Acton Town Hall 2001 - 2002*

As reported in chapter 2, Meyer (2001) provided a correction for PM mass collected using a Partisol 2025 dichotomous sampler because some of the fine fraction was found on the coarse filter. However, it is not clear whether this apportionment is appropriate for species measured by ion chromatography, or any other type of analysis since the size distribution of individual particulate species may differ from that of mass concentrations. It is not considered that this was a problem in respect of the ammonium sulphate concentrations reported above as, apart from a small amount of sulphate which may be associated with sea salt, the majority of sulphate will be present as ammonium sulphate and may be reported as a single concentration in PM10 by combining the measurements on the two filters. However, nitrate is found in both the fine and coarse fractions of PM10 as different species (ammonium nitrate in the fine fraction and sodium nitrate in the coarse fraction). In this study, in the first instance, all measured nitrate has been converted to ammonium nitrate (*1.29) and these measurements are those reported above.

The relationship between fine and coarse mode nitrate (likely ammonium nitrate and sodium nitrate) may nevertheless reveal interesting differences between the two species where it was measured at Acton Town Hall. Nitrate on the coarse filters was apportioned between the coarse and fine fractions using the same conversion equation as the PM mass concentrations. The resulting nitrate on the fine filter was converted to ammonium nitrate (*1.29) and the remaining amount of the nitrate on the coarse filter was converted to sodium nitrate (*1.37).

Figure 4.34 is the time series comparing ammonium nitrate and sodium nitrate at Acton Town Hall (2001 – 2002).

Days when the PM10 daily limit value was exceeded have been disaggregated from high pollution days (Figure 4.35). There were more coarse filters where nitrate concentrations were below the detection limits of the ion chromatography carried out. Those days have been excluded from the following analysis and therefore there may be a small overestimate of sodium nitrate concentrations as a result but only on days when the daily limit value was not exceeded. There were measurable nitrate concentrations on the coarse filters for all the high pollution days (n = 43). On days when the daily limit of value was not exceeded mean ammonium nitrate concentrations were 3.0 (±0.3) μg $m^{-3}$ and sodium nitrate concentrations were 0.9 (±0.1) μg $m^{-3}$ (i.e. approximately 25% of nitrate concentrations were present as sodium nitrate). On high pollution days mean ammonium nitrate concentrations were 10.8 (±1.4) μg $m^{-3}$ and sodium nitrate concentrations were 1.9 (±0.3) μg $m^{-3}$ – see Figure 4.35. Both concentrations increase but ammonium nitrate in the fine fraction increases by a factor of approximately three whilst sodium nitrate increased by a factor of approximately two. Ammonium nitrate remained a key influence on PM mass concentrations on days when the daily limit value was exceeded.

*Figure 4.34* *Time series fine mode nitrate (as ammonium nitrate) and coarse mode nitrate (as sodium nitrate), Acton Town Hall, 2001 - 2002*

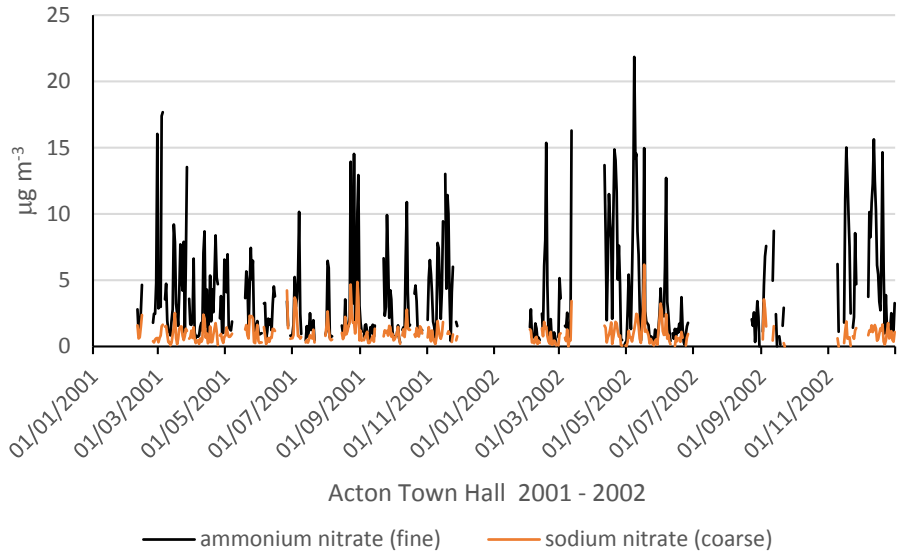
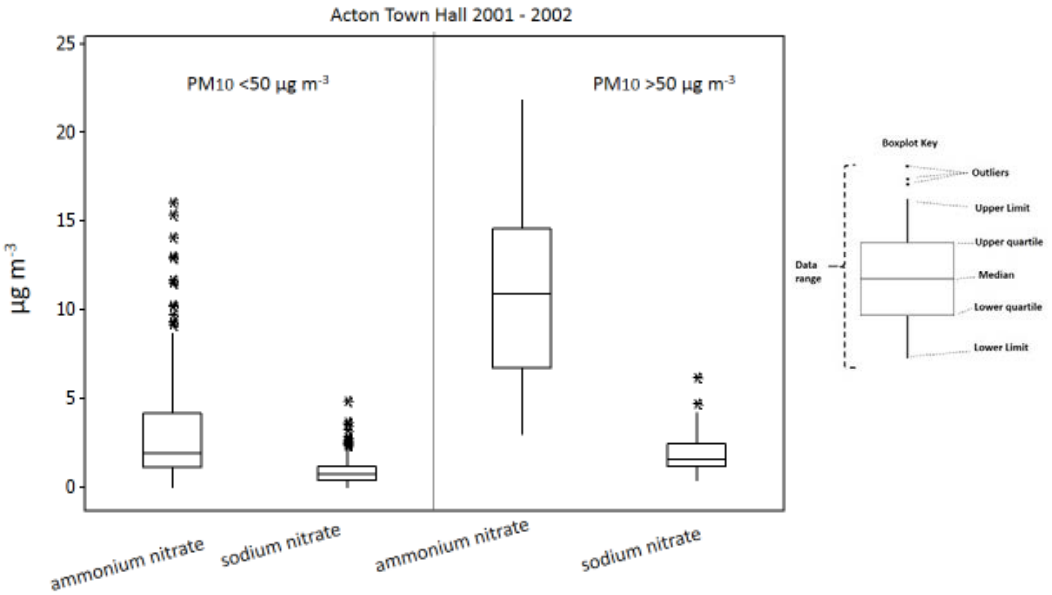



*Figure 4.35* *Boxplots comparing the behaviour of ammonium nitrate and sodium nitrate at Acton ` Town Hall on days when PM10 concentrations were below and above 50 µg m$^{-3}$.*



# SODIUM CHLORIDE

The final anion considered in this chapter is chloride which in the first instance has been converted to sodium chloride from the chloride measurements at all three sampling sites. Understanding chloride measurements is important because the 2008 Directive (2008/50/EC) allows member states to discount days when the daily limit value is exceeded due to natural sources which include sea salt. Ambient sea salt concentrations are based on chloride measurements (Brookes et al., 2012).

Table 4.11 sets out the mass concentrations at each site and Figures 4.36 to 4.38 are the time series at each site. There were no data for either North Kensington or Marylebone Road for 2012 and no data for Marylebone Road for 2011. Figure 4.39 are the boxplots showing the distribution of sodium chloride at each site. Mean concentrations at each site were very similar but the days with maximum concentrations at North Kensington and Marylebone Road seemed to be very high. Unfortunately there were no PM10 or PM2.5 measurements at either site for either of the days with the maximum concentrations but the other anions were also relatively high on those days. An interesting feature is that although the dates were very close, on the commensurate date at the other site (North Kensington/ Marylebone Road) there were not similar high values. Without the PM10 concentrations or other site data it is not possible to know what may have caused these high measurements.

*Table 4.11 Mean and maximum concentrations, sodium chloride, all study sites*

| Site | Sampling period | No of sample days | Mean (95%C.I.) | Maximum (date) |
|---|---|---|---|---|
| | | | sodium chloride ($\mu g\ m^{-3}$) | |
| Acton Town Hall | January 2001 – December 2002 | 404 | 2.5 (2.3,2.7) | 12.9 (4.11.01) |
| North Kensington | 2002 – 2011 | 3114 | 2.4 (2.3,2.44) | 48.9 (19.2.08) |
| Marylebone Road | 2002 - 2010 | 2488 | 2.8 (2.7,3.0) | 46.1 (15.2.08) |

*Figure 4.36 Time series, sodium chloride concentrations, Acton Town Hall 2001 – 2002*

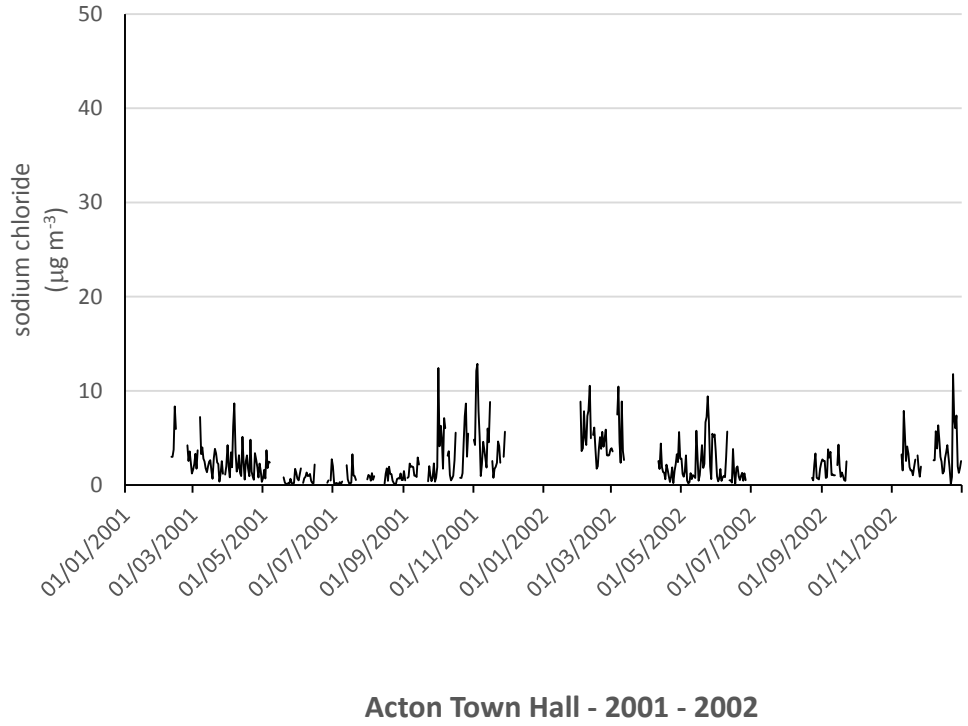



*Figure 4.37 Time series, sodium chloride concentrations, North Kensington, 2002 - 2011*

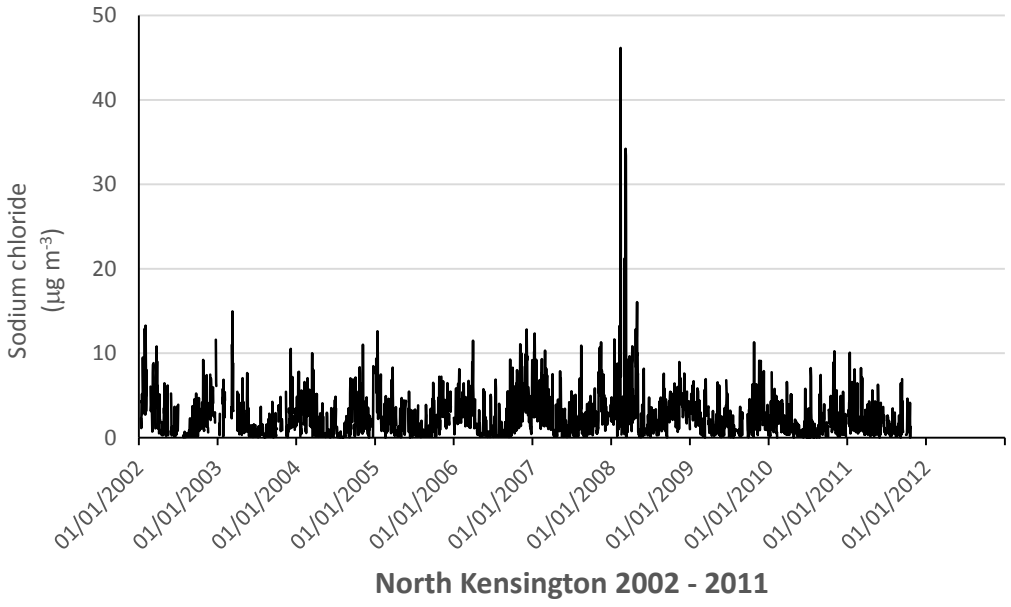


*Figure 4.38 Time series, sodium chloride concentration, Marylebone Road, 2002 - 2010*

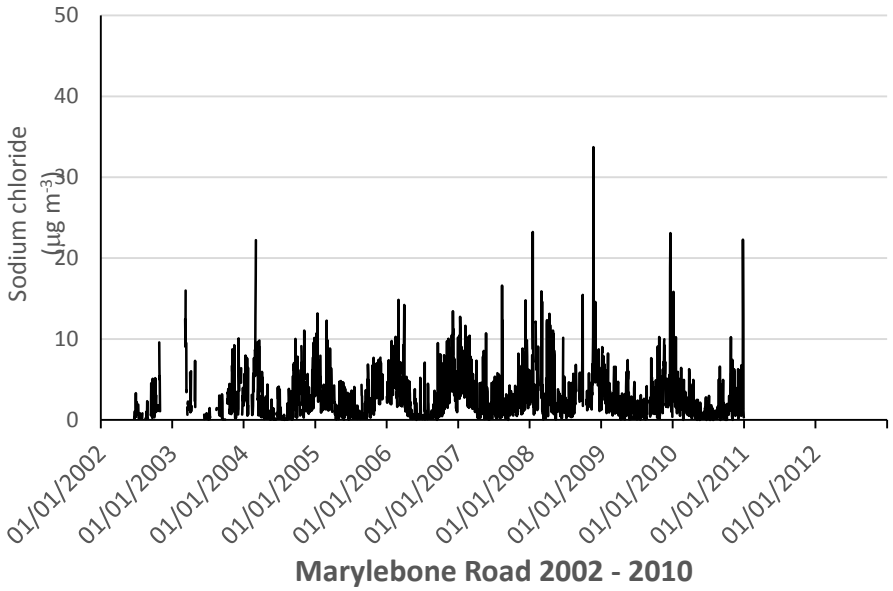
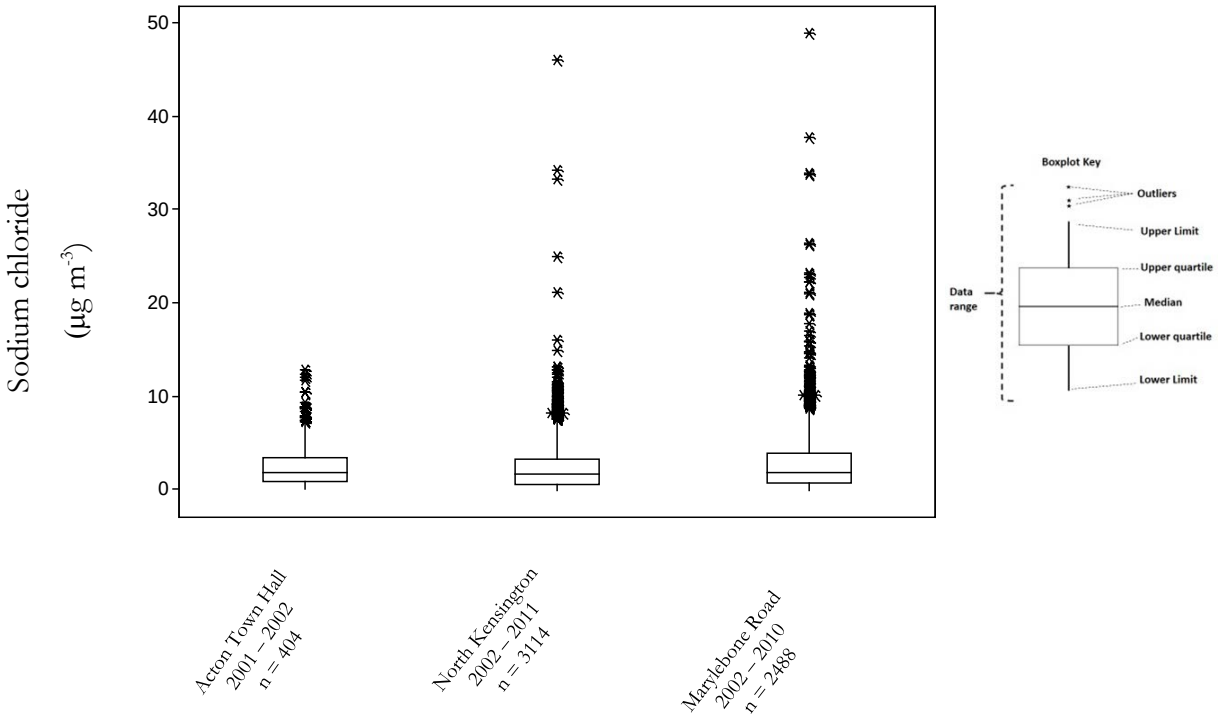



*Figure 4.39 Boxplots comparing concentrations of sodium chloride at each study site*



## *Trend Analysis (sodium chloride)*

Trend analysis for each site is shown in Figures 4.40 – 4.42 and details are set out in Table 4.12 below. There were no significant trends in sodium chloride at any of the sites.

*Table 4.12 Summary of TheilSen trend analysis and statistical significance, sodium chloride*

| sodium chloride | | | | |
|---|---|---|---|---|
| **Site** | **Sampling period** | **No of sample days** | **trend ($\mu g\ m^{-3}$) per year (95% C.I.)** | **p** |
| Acton Town Hall | 2001 – 2002 | 404 | 0.56 (-0.72,1.84) | >0.1 |
| North Kensington | 2002 - 2011 | 3114 | -0.03 (-0.13, 0.05) | >0.1 |
| Marylebone Road | 2002 - 2010 | 2488 | 0.03 (-0.13,0.14) | >0.1 |

*Figure 4.40 TheilSen analysis, sodium chloride, Acton Town Hall 2001 – 2002 (p = >0.1)*

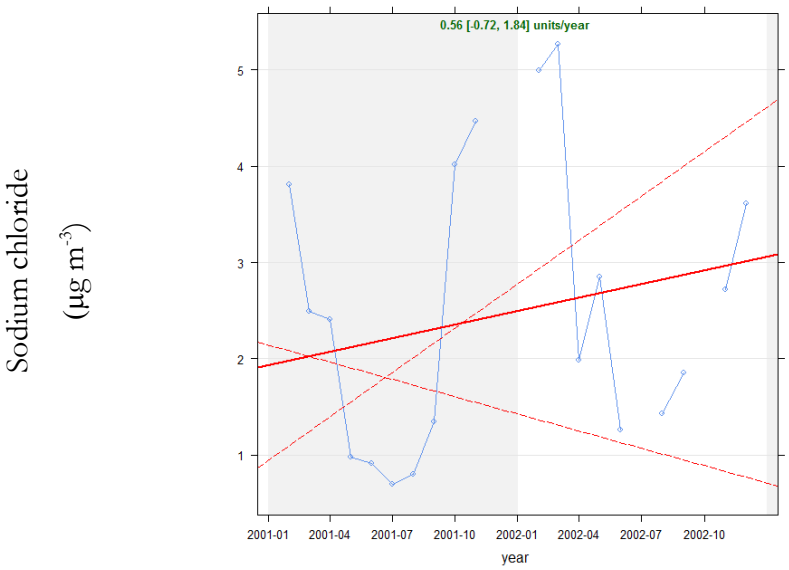


*Figure 4.41* *TheilSen analysis, sodium chloride, North Kensington, 2002 – 2011 (p = >0.1)*

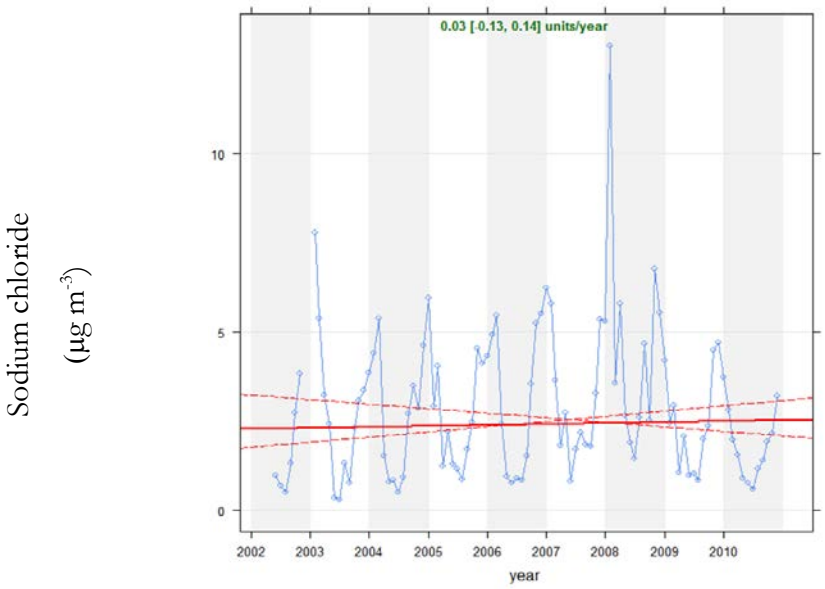
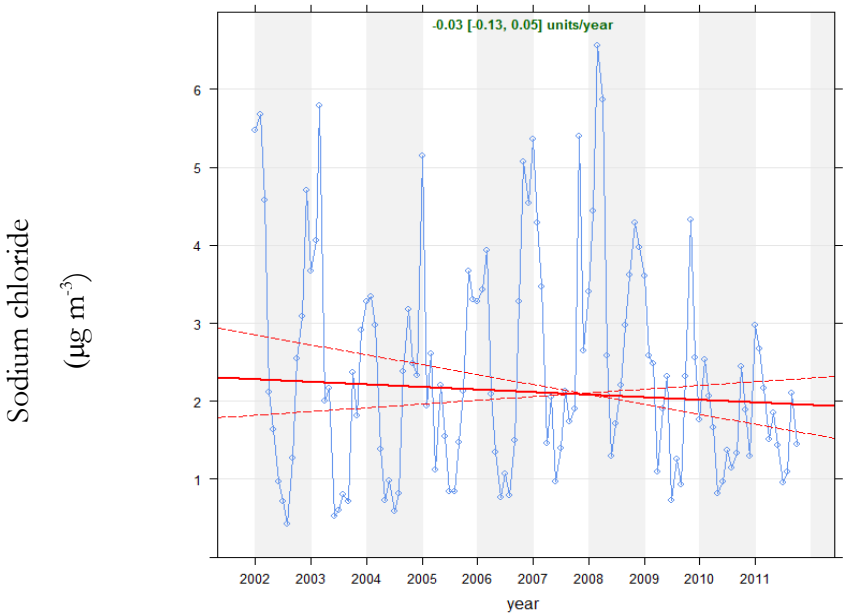



*Figure 4.42* *TheilSen analysis, sodium chloride, Marylebone Road, 2002 – 2010 (p =>0.1)*



## *Day of the week and Monthly Trends (sodium chloride)*

Day of the week trends are set out in Figures 4. 43 to 4.45. There were no clear differences between the mean daily concentrations at each site suggesting that human activity had less influence on these concentrations. The range of daily concentrations at North Kensington was between 2.0 μg $m^{-3}$ (Mondays) to 2.2 μg $m^{-3}$ (Thursdays) whilst at Marylebone Road the range of concentrations was between 2.7 μg $m^{-3}$ (Wednesdays and Thursday) to 3.0 μg $m^{-3}$ on Sundays. The range of concentrations was very similar at both sites but mass concentrations seemed to be higher at Marylebone Road.

Figures 4.46 to 4.48 are the monthly trends. There were clear seasonal differences at each location with lower concentrations noticeable in the summer months suggesting again that natural sources dominate sodium chloride concentrations with winter storms elevating levels of sea-salt concentrations. However, compared to North Kensington, the mean concentrations were higher in the winter months at both Acton Town Hall and Marylebone Road. For example mean concentrations during February months at North Kensington were 3.3 μg $m^{-3}$ whilst at Acton Town Hall and Marylebone Road were 4.7 μg $m^{-3}$ and 4.5 μg $m^{-3}$ respectively. It is possible that this increase was due to road salting which could have occurred at both Acton Town Hall and Marylebone Road but not North Kensington.

*Fig 4.43 day of week variation in sodium chloride, Acton Town Hall 2001 - 2002*

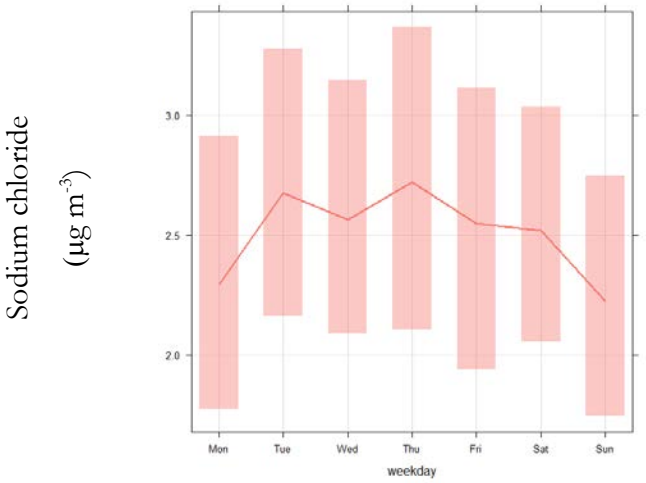



*Fig 4.44 day of week variation in sodium chloride, North Kensington 2002 - 2011*

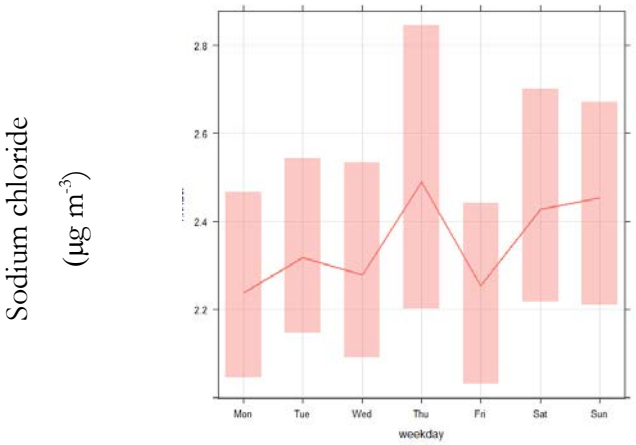



*Fig 4.45 day of week variation in sodium chloride, Marylebone Road, 2002 - 2010*

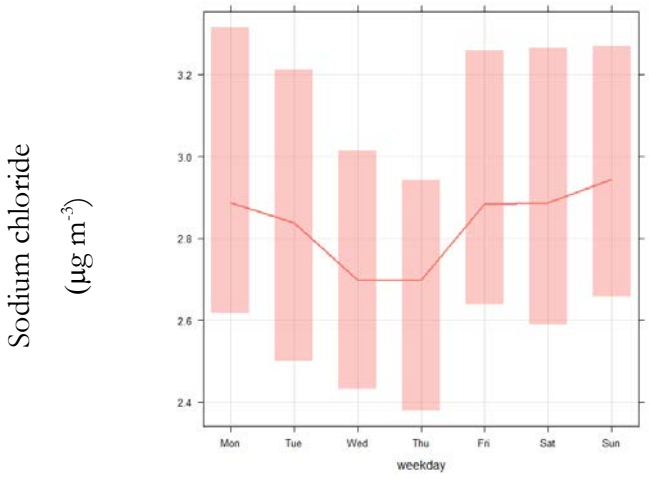


*Fig 4.46 monthly variation in sodium chloride, Acton Town Hall 2001 - 2002*

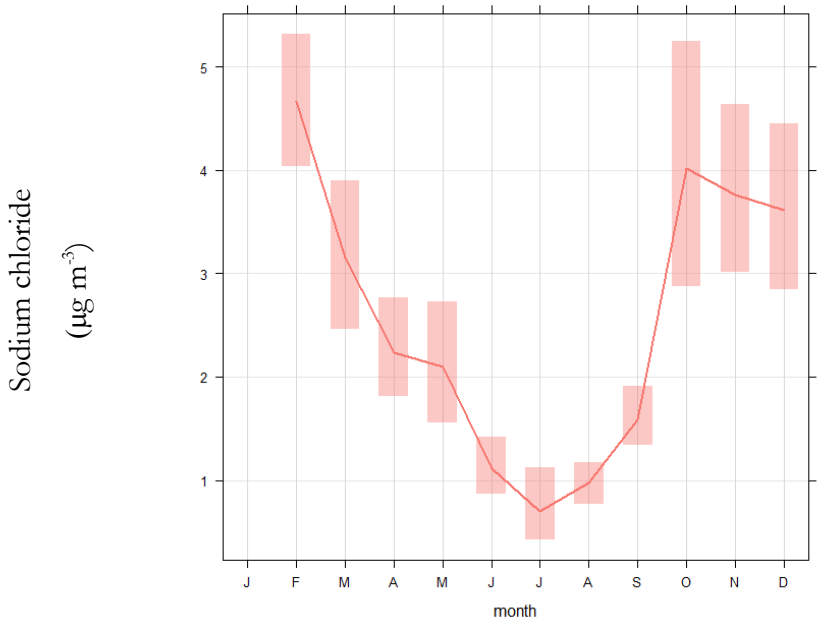



*Fig 4.47 monthly variation in sodium chloride, North Kensington 2002 - 2011*

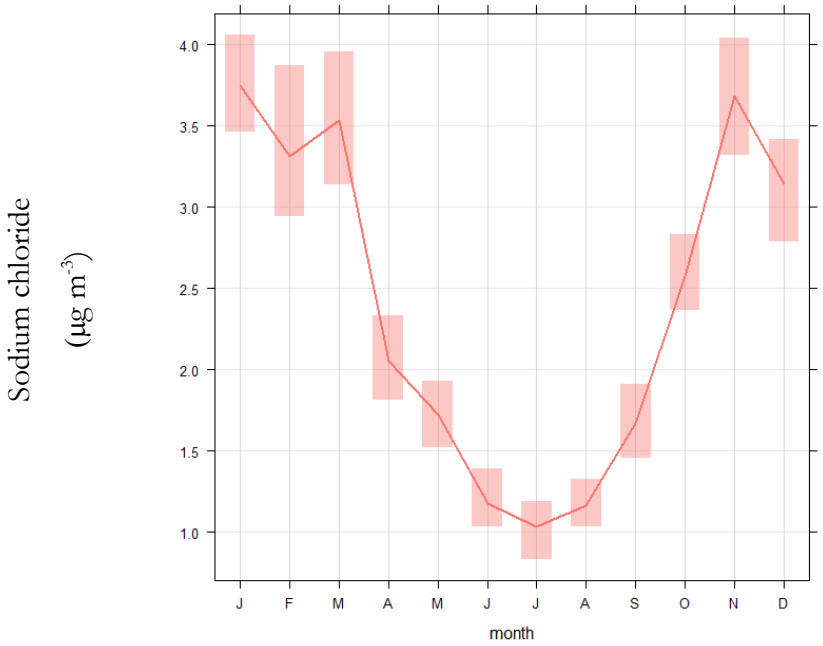
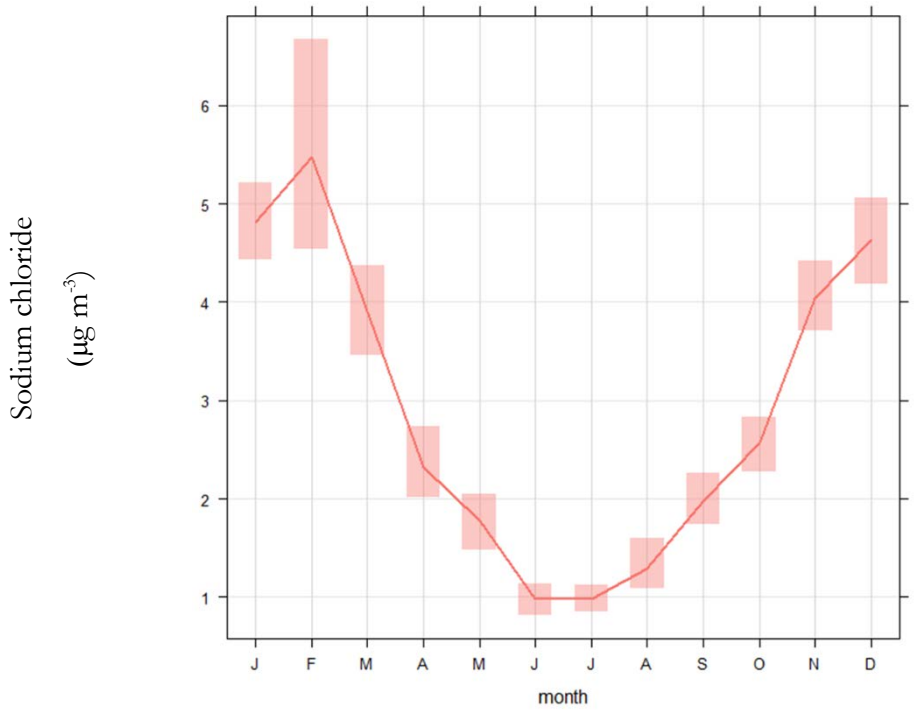


*Fig 4.48 monthly variation in sodium chloride, Marylebone Road, 2002 - 2010*



## *Sodium chloride grouped by PM10 concentrations*

As in the other species described in this chapter mean sodium chloride concentrations have been grouped according to mean PM10 mass concentrations. The same dataset has been used throughout this chapter. It should be noted that there were fewer data available for chloride at Marylebone compared with North Kensington.

As may be seen from Table 4.13, in contrast to ammonium sulphate and ammonium nitrate, the percentage contribution made by sodium chloride reduces as PM10 concentrations rise but there would seem to be differences between the concentrations measured at North Kensington and Marylebone Road, particularly when PM10 mass concentrations were elevated. This is explored in more detail in the next section.

*Table 4.13 mass concentrations of sodium chloride grouped by PM10 concentration 'bin'*

| | **PM10 concentration 'bin'** | | | | | |
|---|---|---|---|---|---|---|
| **Site Sampling period** | **<20 (95% C.I)** | **20 – 30 (95% C.I)** | **30 – 40 (95%C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95%C.I.)** | **>60 (95% C.I.)** |
| | **sodium chloride (µg m$^{-3}$)** | | | | | |
| | Quartz fibre filters | | | | | |
| Acton Town Hall 2001 – 2002 | 2.5 (2.1,2.8) | 3.1 (2.7,3.5) | 2.1 (1.7,2.5) | 1.4 (0.9,1.9) | 1.9 (1.1,2.6) | 3.5 (0.9,6.0) |
| %age contribution to PM10 concentration | 15% | 12% | 6% | 3% | 4% | 5% |
| No of sample days | 81 | 154 | 91 | 35 | 30 | 13 |
| North Kensington 2002 - 2006 | 2.2 (1.9,2.5) | 2.3 (2.1,2.6) | 1.9 (1.5,2.2) | 1.3 (1.0,1.6) | 2.4 (1.6,3.3) | 2.8 (1.5,4.1) |
| %age contribution to PM10 concentration | 14% | 9% | 6% | 3% | 4% | 4% |
| No of sample days | 192 | 301 | 143 | 59 | 19 | 23 |
| Marylebone Road 2002 - 2006 | 2.6 (1.7,3.4) | 2.0 (1.6,2.3) | 2.5 (2.1,2.8) | 2.7 (2.3,3.1) | 2.8 (2.2.3.3) | 3.0 (2.2,3.7) |
| %age contribution to PM10 concentration | 16% | 8% | 7% | 6% | 5% | 4% |
| No of sample days | 21 | 113 | 218 | 188 | 108 | 89 |
| | Emfab$^{TM}$ filters | | | | | |
| North Kensington 2009 – 2011 | 1.8 (1.6,1.9) | 1.8 (1.5,2.2) | 2.1 (1.5,2.6) | 1.6 (1.0,2.1) | 1.8 (0.8,2.7) | |
| %age contribution to PM10 concentration | 15% | 8% | 6% | 4% | 3% | - |
| No of sample days | 374 | 88 | 32 | 20 | 9 | - |
| Marylebone Road 2009 - 2010 | 1.6 (1.3,1.9) | 1.9 (1.5,2.2) | 2.2 (1.8,2.5) | 3.0 (2.1,3.9) | 2.7 (1.9,3.4) | 3.4 (2.3,4.4) |
| %age contribution to PM10 concentration | 10% | 8% | 6% | 7% | 5% | 5% |
| No of sample days | 77 | 111 | 144 | 72 | 23 | 19 |

Table 4.14 and Figures 4.49 and 4.50 compare sodium chloride concentrations at Marylebone Road and North Kensington grouped according to PM10 mass concentrations at Marylebone Road. When PM10 mass concentrations at Marylebone Road were below 50 μg $m^{-3}$ during 2002 to 2006 and below 40 μg $m^{-3}$ after 2009 (i.e. on the majority of days) sodium chloride concentrations were similar between the sites. However once PM10 mass concentrations began to rise, mass concentrations of sodium chloride were higher at Marylebone Road and were in the region of 50% more. There would appear to have been some roadside enhancement and this is illustrated in Figures 4.49 and 4.50.

*Table 4.14* *Same day mean sodium chloride concentrations, Marylebone Road and North Kensington, based on mean PM10 concentration 'bins' at Marylebone Road 2002 – 2006, and 2009 - 2010*

| | **PM10 concentration 'bin' at Marylebone Road** | | | | | |
|---|---|---|---|---|---|---|
| **Site** | **<20 (95% C.I)** | **20 – 30 (95% C.I)** | **30 – 40 (95%C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95%C.I.)** | **>60 (95% C.I.)** |
| | **sodium chloride μg $m^{-3}$)** | | | | | |
| | **2002 - 2006** | | | | | |
| No of sample days | 21 | 113 | 218 | 188 | 108 | 89 |
| Marylebone Road | 2.6 (1.7,3.4) | 2.0 (1.6,2.3) | 2.5 (2.1,2.8) | 2.7 (2.3,3.1) | 2.8 (2.2.3.3) | 3.0 (2.2,3.7) |
| North Kensington | 2.6 (1.8,3.3) | 1.8 (1.5,2.1) | 2.1 (1.8,2.4) | 2.4 (2.0,2.8) | 2.1 (1.7,2.5) | 2.2 (1.7,2.7) |
| | **2009 - 2010** | | | | | |
| No of sample days | 77 | 111 | 144 | 72 | 23 | 19 |
| Marylebone Road | 1.6 (1.3,1.9) | 1.9 (1.5,2.2) | 2.2 (1.8,2.5) | 3.0 (2.1,3.9) | 2.7 (1.9,3.4) | 3.4 (2.3,4.4) |
| North Kensington | 1.6 (1.2,1.9) | 1.6 (1.3,1.8) | 2.0 (1.7,2.3) | 1.9 (1.5,2.3) | 1.9 (1.2,2.6) | 2.1 (1.4,2.7) |

*Figure 4.49* *same day mean sodium chloride concentrations, Marylebone Road and North Kensington, based on mean PM10 concentration 'bins' at Marylebone Road 2002 - 2006*

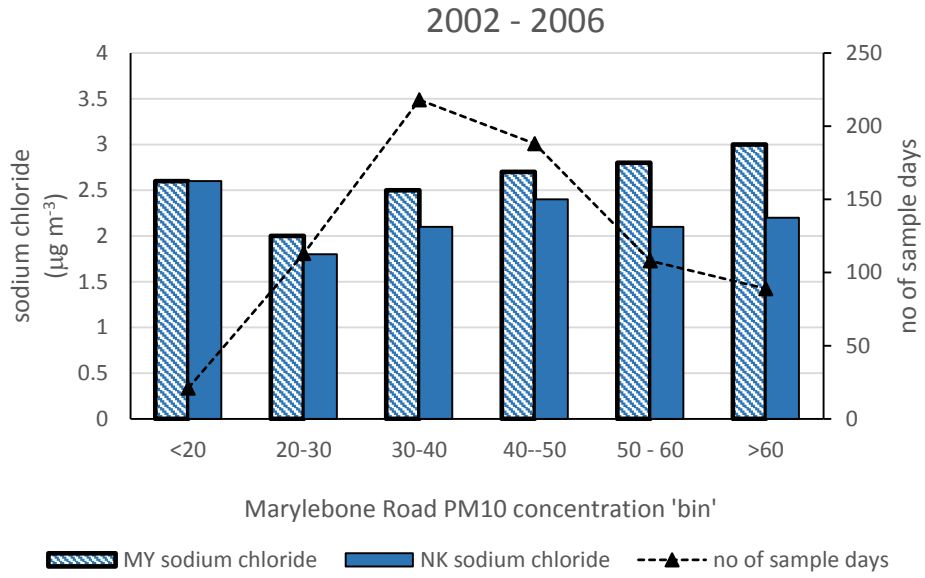
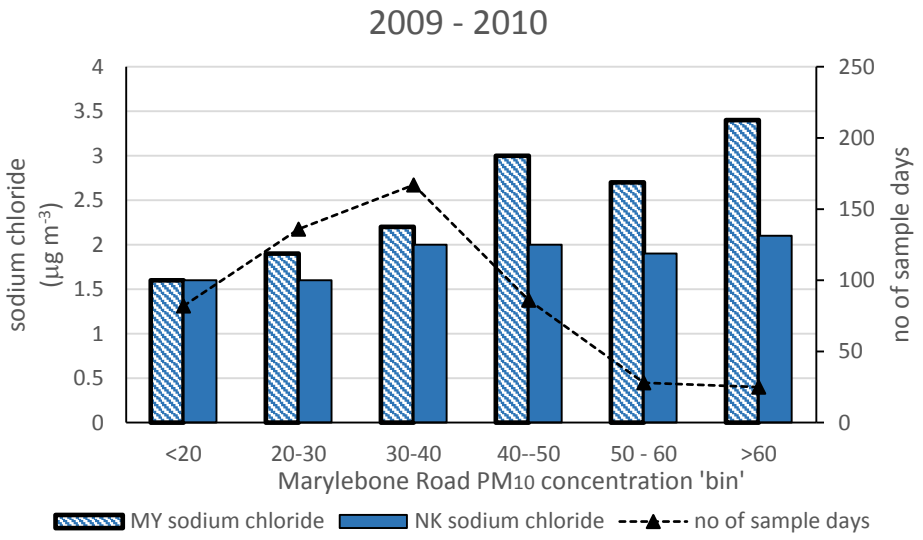



*Figure 4.50* *same day mean sodium chloride concentrations, Marylebone Road and North Kensington, based on mean PM10 concentration 'bins' at Marylebone Road 2009 - 2010*

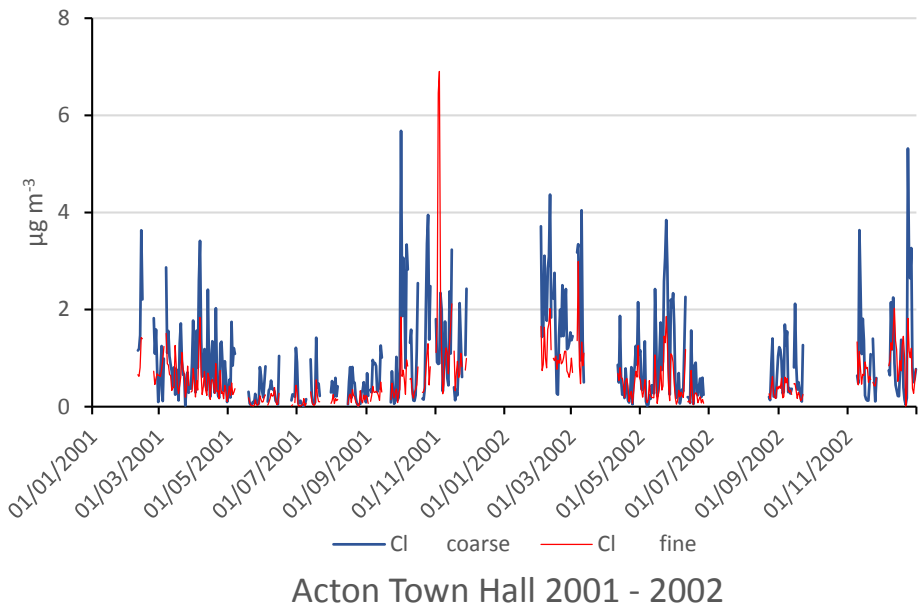


# Acton Town Hall – chloride in the fine and coarse PM fraction

All of the chloride measurements used in the above analysis were converted to sodium chloride (*1.65) and were considered to be present as sea salt. The use of the dichotomous sampler at Acton Town Hall has provided the opportunity to consider whether chloride in the fine fraction might be present due to secondary displacement of other ions (as found by White, 2008 and Beuck et al. 2011) or primary emissions of chloride from coal burning for example as suggested by Jones et al. (2010). Figure 4.51 compares the concentrations of chloride measured on the fine and coarse filters without converting to sodium chloride or any other species. As discussed earlier some of the fine particles in the PM10 mass measured with a dichotomous sampler is collected on the coarse filter and there is an algorithm available to deal with this (Meyer, 2001) which was used in the previous section to distinguish between ammonium nitrate and sodium nitrate. However, if the same apportionment was made in respect of the chloride measurements this might over emphasise the contribution made by chloride in the fine fraction.

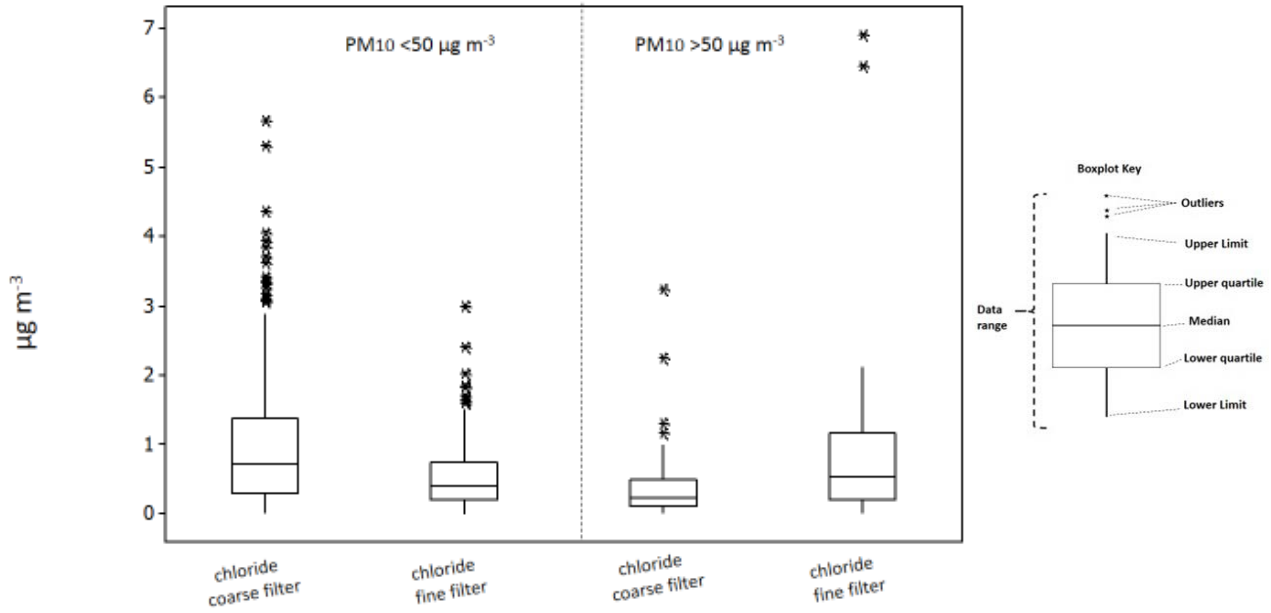
It is clear from Figure 4.51 that chloride measurements on the fine filter were generally lower than chloride measurements on the coarse filter but on 3 and 4 November 2001 overall mass concentrations from the study site exceeded the daily limit value and, as may be seen from Figure 4.51, unusually high peaks of chloride were detected on the fine filters. Vecchi et al. (2008) carried out an interesting study of PM immediately after Italy won the football world cup in 2006 with subsequent fireworks in Milan and found increases in chloride. They attributed this to the use of barium to create the green colour in the fireworks and hence the production of $Ba(ClO_3)_2$. It is possible that the chloride measured in this study on 3 and 4 November 2001 may also be mainly attributable to nearby fireworks set off to celebrate Guy Fawkes Night (traditionally in the UK on 5 November as well as the nearest weekends).

*Figure 4.51 comparison of chloride measurements, fine and coarse mode, Acton Town Hall, 2001 - 2002*




Chloride concentrations in each size fraction have been disaggregated between days when the PM10 daily limit value was exceeded and other days and are illustrated by way of boxplots in Figure 4.52. These plots reveal an interesting feature. On days when the daily limit value was not exceeded (n = 361) the mean concentration of chloride measured on the coarse filters was 1.0(±0.1) µg $m^{-3}$ and on the fine filter 0.5(±0.05) µg $m^{-3}$. The concentrations reverse on days when the daily limit value was exceeded such that the mean concentration on the coarse filters was 0.5 (±0.1.5) µg $m^{-3}$ and on the fine filters was 1.0(±0.4) µg $m^{-3}$. The 95% confidence limits were greater on days when the daily limit value was exceeded but the sample number was also lower. Nevertheless there is evidence to suggest that not all of the chloride in PM10 should be attributed to sea-salt and may be from anthropogenic sources such as power stations (HCl) and fireworks. As discussed in chapter 1, in the UK chloride concentrations are used to calculate the contribution by sea-salt for the purposes of adjusting the number of days when the daily limit value is exceeded due to 'natural sources' and not caused by human activities (Brookes et al, 2012)

*Figure 4.52* *Boxplots of fine and coarse mode chloride at Acton Town Hall, 2001 – 2002 comparing days when the daily limit value of 50 μg m$^{-3}$ was exceeded with other days.*



# Summary

Concentrations of ammonium sulphate, ammonium nitrate and sodium chloride in ambient particulate matter have been calculated and compared at three locations in London: Acton Town Hall, North Kensington and Marylebone Road during the period 2001 and 2012. Overall trend analysis indicated that there were no changes in either ammonium nitrate or sodium chloride concentrations during the study period but this was not the case in respect of ammonium sulphate. There seemed to be a step change in concentrations in ammonium sulphate at the beginning of 2008 which is confirmed by considering both trend analysis and mean concentrations of ammonium sulphate during the periods 2002 to 2006 and 2009 to 2012 at both North Kensington and Marylebone Road. The sale of ultra-low sulphur fuel became obligatory for the majority of retail outlets at the end of 2007 and the first phase of the Low Emission Zone was introduced early in 2008. It seems likely that the introduction of ultra-low sulphur fuel had an important influence on concentrations of ammonium sulphate in ambient particulate matter. However, there is evidence that this reduction has not been sustained and this may be due to an increase in regional sources, such as shipping, regional electricity generation and increases in the numbers of diesel vehicles. A comparison with co-located concentrations of precursor species such as sulphur dioxide, such as that carried out by Jones and Harrison (2011), could be used in future work to consider this in more detail.

Seasonal differences were noticeable in all three species. They were all at their lowest concentrations in the summer months, although prior to 2006 this was less noticeable in ammonium sulphate concentrations. Highest concentrations of ammonium sulphate and ammonium nitrate occurred in the spring months. It is probable that these were as a result of long range transport from continental Europe which has also been reported elsewhere (see for example Smith et al., 2001) and attributable to increased ammonia production from different land management practices in the Spring.

The contribution of each species to PM10 concentrations between sites has been compared. Unfortunately as a result of the filter change from quartz to Emfab in 2007 and the consequent apparent reduction in PM concentrations it is only possible to distinguish site

differences between 2002 and 2006 and after 2009 but not to compare concentrations between the two time periods. The concentrations were grouped by PM10 10 μg $m^{-3}$ concentration 'bins' for detailed analysis. A summary is also provided in Table 4.15 below where all days at North Kensington and Marylebone Road are compared with days when the daily limit value was not exceeded and days when the daily limit value was exceeded.

Before 2006 concentrations of ammonium sulphate increased significantly at all sites on days when the daily limit value was exceeded but its percentage contribution to overall PM10 concentrations remained constant. However the percentage contribution was lower at Marylebone Road (11%) -when compared to North Kensington (15/16%) and Acton Town Hall (14 – 16%). Ammonium nitrate concentrations also increased significantly on days when the daily limit value was exceeded and its percentage contribution also increased at North Kensington and Marylebone Road. However the percentage contribution was again higher at North Kensington (23%) compared to Marylebone Road (15%). Sodium chloride exhibited the opposite behaviour to both ammonium sulphate and ammonium nitrate at all sites and its percentage contribution to PM10 concentrations dropped at all sites (although less so at Marylebone Road). At Marylebone Road the three species contributed 27% to PM10 concentrations on days when the daily limit value was not exceeded and 31% on high pollution days. At North Kensington all species contributed 40% on days when PM10 mass concentrations were below the daily limit value and 43% on high pollution days. At both sites, the increases in ammonium nitrate were balanced by the decreases in sodium chloride on high pollution days.

*Table 4.15* *Summary of ammonium sulphate, ammonium nitrate and sodium chloride mean concentrations and their percentage contribution to PM10 concentrations at Marylebone Road and North Kensington*

| | Marylebone Road 2002 – 2006 (quartz filter substrate) | | | | | |
|---|---|---|---|---|---|---|
| | All days | | Daily limit value not exceeded | | Daily limit value exceeded | |
| | Mean ($\mu g\ m^{-3}$) | % | Mean ($\mu g\ m^{-3}$) | % | Mean ($\mu g\ m^{-3}$) | % |
| No of sample days | 737 | | 540 | | 197 | |
| PM10 | 42.8 (41.7 ,44.0) | | 35.4 (34.7,36.1) | | 63.2 (61.2,65.2) | |
| Ammonium sulphate | 4.6 (4.4,4.8) | 11% | 3.7 (3.5,3.9) | 10% | 7.0 (6.5,7.5) | 11% |
| Ammonium nitrate | 5.1 (4.8,5.5) | 12% | 3.6 (3.4,3.9) | 10% | 9.3 (8.4,10.3) | 15% |
| Sodium chloride | 2.6 (2.4,2.8) | 6% | 2.5 (2.2,2.7) | 7% | 2.9 (2.4,3.3) | 5% |
| | | | | | | |
| | North Kensington 2002 – 2006 (quartz filter substrate) | | | | | |
| No of sample days | 737 | | 693 | | 44 | |
| PM10 | 27.8 (26.9,28.7) | | 25.5 (24.9,26.2) | | 63.7 (60.1,67.3) | |
| Ammonium sulphate | 4.2 (4.0,4.4) | 15% | 3.8 (3.6,4.0) | 15% | 10.1 (8.8,11.4) | 16% |
| Ammonium nitrate | 4.6 (4.2,4.9) | 17% | 3.9 (3.7,4.2) | 15% | 14.7 (12.5,17.0) | 23% |
| Sodium chloride | 2.1 (2.0,2.3) | 8% | 2.1 (2.0,2.3) | 8% | 2.6 (1.8,3.4) | 4% |
| | | | | | | |
| | Marylebone Road 2009 - 2011 ( Emfab™ filter substrate) | | | | | |
| No of sample days | 523 | | 470 | | 53 | |
| PM10 | 33.0 (32.0,34.2) | | 30.0 (29.1,31.0) | | 60.0 (57.8,62.2) | |
| Ammonium sulphate | 3.0 (2.8.3.2) | 9% | 2.6 (2.5,2.8) | 9% | 6.3 (4.9,7.7) | 11% |
| Ammonium nitrate | 4.6 (4.1,5.1) | 14% | 3.5 (3.2,3.8) | 12% | 14.7 (11.1,18.2) | 25% |
| Sodium chloride** | 2.2 (2.0,2.4) | 7% | 2.1 (1.9,2.4) | 7% | 3.0 (2.4,3.6) | 5% |
| | | | | | | |
| | North Kensington 2009 – 2011 ( Emfab™ filter substrate) | | | | | |
| No of sample days | 523 | | 514 | | 9 | |
| PM10 | 17.5 (16.6,18.3) | | 16.8 (16.0,17.5) | | 56.6 (51.3,61.9) | |
| Ammonium sulphate | 2.8 (2.7,3.0) | 16% | 2.8 (2.6,2.9) | 17% | 6.5 (5.3,7.6) | 11% |
| Ammonium nitrate | 3.9 (3.5,4.2) | 22% | 3.6 (3.3,3.8) | 21% | 21.4 (16.2,26.6) | 38% |
| Sodium chloride | 1.8 (1.6,2.0) | 10% | 1.8 (1.6,2.0) | 11% | 1.8 (0.8,2.7) | 3% |

****** No sodium chloride measurements available, Marylebone Road in 2011.
There were 444 sample days in this subset of which 42 were days when the daily limit value was exceeded.

After 2009, the concentrations of ammonium sulphate are lower, particularly on days when the daily limit value was not exceeded, but the percentage contribution remained similar (9 - 11%) as the period between 2002 and 2006. However ammonium sulphate concentrations at North Kensington on high pollution days were not only lower but also made a smaller percentage contribution (11% compared to 16% previously). Ammonium nitrate concentrations at North Kensington were similar to Marylebone Road on days when the daily limit value was not exceeded but made a higher contribution to overall PM10 concentrations (22% compared to 14%). On high pollution days the contribution made by ammonium nitrate concentrations was 38% compared to 25% at Marylebone Road but this may be caused by fewer days in this category (n = 9) with a greater range of concentrations. Sodium chloride continued to make lower contributions to PM10 mass concentrations on high pollution days compared to other days at both sites although the percentage reduction was more noticeable at North Kensington. At Marylebone Road all species contributed to 28% of overall PM10 concentrations on days when the Daily Limit Value was not exceeded and this increased to 41% on high pollution days. At North Kensington there was a less obvious distinction between the percentage contributions although it was overall higher than Marylebone Road (48% on days when the daily limit value was not exceeded compared to 51% on high pollution days). The increased percentage contribution made by ammonium nitrate on high pollution days at North Kensington was balanced by reductions in the percentage contribution made by ammonium sulphate and sodium chloride.

It seemed from the above analysis that the three inorganic sources, ammonium sulphate, ammonium nitrate and sodium chloride, made lower overall contributions to PM10 mass at Marylebone Road compared to North Kensington and this was confirmed by comparing concentrations of each species on the same days between the two sites. It is concluded therefore that other, probably local, sources are responsible for a greater percentage of PM10 mass at Marylebone Road compared to North Kensington. It seems possible that these sources could be linked to traffic emissions and this is explored further in the next two chapters.

# Chapter 5

# Determining equivalent black carbon concentrations based on the light absorbing properties of PM samples

## Introduction

In London, as set out in chapter 1, particulate carbon present in the atmosphere has been routinely measured at two sites, Marylebone Road and North Kensington, since 2007. At both sites these carbon concentrations have been measured by two different methods. 'Real-time' black carbon (BC) concentrations have been determined by Magee aethalometers (model AE22). Elemental carbon and organic carbon (EC/OC) concentrations have been determined using the NIOSH-TOT method on time resolved (24 hour) samples collected using a Partisol 2025 gravimetric sampler on a quartz fibre filter. Details of daily concentrations ($\mu g\ m^{-3}$) are publicly available via the Defra website (uk-air.defra.gov.uk). Prior to this black smoke measurements ($BS_{(British)}$) were made at a number of sites in London, including Marylebone Road, and, as also discussed in chapter 1, were based on the loss of reflectance from a stain on a filter also collected over a 24 hour period. Details of these concentrations are also available via the Defra website and the Londonair website (www.londonair.org.uk) maintained by ERG at KCL.

$BS_{(British)}$ was described by Moosmüller et al. (2009) as the "first (unknowing) measurement method of aerosol light absorption".

APEG (1999) state that, mass for mass, diesel particles have a blackening effect three to four times greater than coal emissions and it is diesel particles from traffic sources which would nowadays be expected to the be main staining source on a filter in an urban environment. Diesel particles are much smaller in diameter than particles from coal combustion and any conversion factor based on a higher use of coal than diesel will over-estimate the total amount of PM. AQEG (2005) noted that between 1990 and 2002 London sites showed the "smallest black smoke trends due to a significant contribution … from diesel road traffic."

Heal et al. (2000) considered trends in PM in Edinburgh from 1992 to 1997 utilising black smoke measurements from two sites in Edinburgh to represent the primary fraction. They went on (2005a, 2005b) to use co-located black smoke and Partisol PM samplers in a further study in Edinburgh from September 1999 to September 2000 concluding that black smoke 'or some updated measure of particle "darkness" remains a relevant measure of air pollution' and that the combination of PM and black smoke measurements can provide insight into controlling particle concentrations.

There have been a number of air quality studies which have used the light absorbing properties of carbon on a filter to determine an absorption coefficient using the calculation in ISO 9835 (1993) on the basis that this measurement may be used as a proxy for elemental carbon in the atmosphere and hence an indicator of diesel traffic influences (see, for example, Hoek et al. (1997) Kinney et al. (2000), Patuszka et al. (2003), Smargiassi et al. (2005), Van Roosbroeck et al. (2006) ).

During the 1990's a sequence of studies were carried out in the Netherlands. Roorda-Knape et al. (1998) compared the absorption coefficients of Teflon filters sampled in 1995 using Harvard Impactors (PM10) with results from the traditional black smoke method and found they were highly correlated ($r^2$ 0.94). Fischer et al. (2000) sought to clarify the differences in outdoor and indoor exposures in a study in Amsterdam in 1995 and used the absorption coefficient of both PM10 and PM2.5 filters as a proxy for elemental carbon. They did not carry out any conversion to a mass concentration because they acknowledged that the transformation in the OECD protocol is "filter specific and no transformation is available for the present filter." Elemental carbon was not measured directly in either of these studies. By contrast a study carried out by Janssen et al. (2001) in 1997/98 measured the absorption coefficient of PM2.5 filters (Teflon) collected over a period of one week, again using Harvard Impactors, and compared it with elemental carbon measured on a subset of quartz filters collected at the same time. Again the measurements were highly correlated with a reported r value of 0.92.

Adams et al. (2002) also derived a site specific calibration for the conversion of the absorption coefficient based on Teflon filters (PM2.5) to elemental carbon, in a study carried out in London during 1999 and 2000, assessing the personal exposure of several different categories of road users.

Götschi et al. (2005) compared the reflectance of PM2.5 filters from 21 European locations, including two in the UK, using reflectance as a surrogate measure for elemental carbon and hence an indicator of diesel traffic. Where measurements were taken at different locations within one city (Antwerp) the two locations had 'pronounced' differences between the reflectance measurements (2.9 versus 1.7 absorption coefficient $10^5$ $m^{-1}$). City to city variations were also reported and it was concluded that this probably reflected the varying contributions made by local emissions. The same dataset was used by Künzli et al. (2006) when seeking to identify a surrogate measurement for PM redox activity for use in epidemiology studies. Correlations between absorbance and redox activity were weak but nevertheless the value of using the absorption coefficient as a surrogate for elemental carbon across multiple sites in various studies was demonstrable.

Eeftens et al. (2012) investigated relationships between air pollution and health in 16 European countries. They used the reflectance of Teflon filters converted to an absorption coefficient as set out in ISO (1993) as an exposure surrogate without converting to any equivalent mass concentration.

Chow et al. (2010) compared light attenuation from filter light transmission through more than 180,000 Teflon filters from nearly 200 US locations collected between 1987 and 2006 with EC measurements determined using the IMPROVE-TOR method, and demonstrated the feasibility of using light attenuation as a surrogate for EC. They also made the point that greater accuracy is achieved using a site-specific mass extinction coefficient "derived from a period with collocated EC measurements".

The studies reported in the above paragraphs used the absorption coefficient of Teflon filters and some then went on to compare the coefficient with elemental carbon measured on co-located quartz filters. Reflectance from the quartz fibre filters was not directly measured. However in a study in Ireland (Eire) PM sampling was carried out at a number of sites from July 2001 to December 2002 using Partisol 2025 dichotomous samplers (Yin et al., 2005). Quartz fibre filters were 'deployed simultaneously' as PTFE filters and an absorption coefficient determined using an EEL reflectometer. A "very strong correlation ($r^2$= 0.99 – 1.00) was observed for the light absorption data between quartz and PTFE filters".

Bond and Bergstrom (2006) note, however, that "despite a long history of using absorption as a surrogate for mass, difficulties in establishing the relationship between the two still exists."

Janssen et al. (2011) evaluated the value of measuring black carbon particles by reviewing many of the above studies and concluded that it is a valuable additional air quality indicator.

# Comparison between Black Smoke and Black Carbon concentrations

The Black Smoke network in the UK was based on measurements of reflected light from a stained filter (Whatman No 1, Maidstone, UK) as described in chapter 1. The measurements of the stain expressed as a percentage were obtained from a reflectometer such as the one described in chapter 2 based on the method in the 'UK Smoke and Sulphur Dioxide Network Instruction Manual' (AEAT, 1999). Mass concentration measurements were derived using a quartic equation set out in BS1747, Part 2 (1969). These measurements were not the same as black smoke measurements in the rest of Europe which were based on a calibration curve set out in OECD publication number 1793 (1963). To achieve equivalence $BS_{(British)}$ needed to be multiplied by 0.85.

In 1993 a further BS 1747 Part 11 (eleven) was issued alongside a revised ISO standard 9835:93. In these standards a revised Black Smoke Index was proposed based on Lambert's Law (ln (Ro/R), where Ro = the intensity of reflected light from the surface of a clean paper; and R = the intensity of reflected light from the surface of a stained paper). Heal and Quincey (2012) derived a $BSI_{(British)}$ calibration, based on these equations and earlier work (Quincey, 2007 and Quincey et al., 2011), in the following form:

$$\mathbf{BSI_{(British)} = 95.6 \ln(Ro/R) (1 + 2.0 \ln(Ro/R))} \qquad \textbf{(Equation 5.1)}$$

Measurements made on an aethalometer are, in the first instance, also based on Beer-Lambert's law. Full details are given in the Operator's Manual (Hansen, 2005). In summary "Optical Attenuation" (ATN) is defined as:

$$ATN = 100 * \ln (Io/I)$$

where $Io$ is the light intensity transmitted through an unexposed blank filter

and $I$ is light transmitted through an exposed filter

Hansen (2005) advised that the factor of 100 was "for numerical convenience". Black carbon (BC) (μg $m^{-3}$) is determined by dividing ATN by the specific mass extinction coefficient ($\sigma_{ATN}$) ($m^2 g^{-1}$), often simply referred to as "sigma", and multiplied by A/V (where A equals the surface area of the sample filter and V = the volume of air sampled). Sigma is wavelength dependent and not a constant. Aethalometers in use in the UK have an inbuilt sigma of 16.6 $m^2$ $g^{-1}$ for BC measurements made when the light source (λ) = 880 nm (i.e. in the infrared wavelength). This sigma value was determined by Magee Scientific by experimentation (based on "the Malissa-Novakov methods for 'BC' determination published by Gundel, Dod et al.(sic)") as set out in its manual (Hansen, 2005). Hansen (2005) noted that the sigma would be different if ATN were to be calibrated against EC measured using the TOR method (12.6 $m^2 g^{-1}$). Hansen also noted that if EC measurements were determined using the TOT method then a further different sigma would be required but did not provide a suggested value.

A number of studies (see, for example, Weingartner et al., 2003, Arnott et al., 2005, and Virkkula et al., 2007) reported that the rate of change of light transmission was not in fact a linear response on filter samples. Lack et al. (2014) summarise the 3 principal factors which influence this lack of linearity:

1. **Multiple light scattering within the filter**: incident light may be scattered by unloaded filter substrate and increase the sample path. This would vary between different types of substrate.
2. **Filter loading**: as more particles are collected on the filter the optical sampling path is decreased leading to bias in the final calculation. This will vary depending on the amount of deposit on the filter.
3. **Particle scattering**: as the filter becomes loaded there is an increase in the amount of light scattering particles leading to incident light being scattered in any direction. This could lead to higher filter reflectance and/or more opportunities for light to be absorbed by other particles. This will vary on the atmospheric particle mix.

Collaud Coen et al. (2010) also described the same three processes and provided a summary of various proposed correction factors to quantify these effects. Gundel et al. (1984) also noted this effect when measuring attenuation using a laser transmission method. Virkkula et al. (2007) described a simple method for correcting and quantifying these effects in the following terms:

**BC(corrected) = (1 +k ATN) * BC (noncorrected) (Equation 5.2)**

where k is an empirically derived constant often referred to as a loading (or shadowing) effect correction.

Virkkula et al. (2007) then provide a further correction which takes in to account the filter changes when the filter spot has reached a pre-set limit. The correction suggested by Virkkula et al. (2007) has been applied to reported BC concentrations from aethalometers in the UK, operated as part of the BC Network (see chapter 1 for details). The correction factor varies by site and time. The daily correction factor for Marylebone Road was reported in the region of 0.007% (Butterfield, 2013, pers comm).

Heal and Quincey (2012) noted the similarity between equations (5.1) and (5.2) above and stated that "the black smoke method is analogous to the black carbon aethalometer method …" although with different mass extinction coefficients and 'k' shadowing corrections. Heal and Quincey (2012) went on to derive a BS to BC conversion in the following form:

$$\mathbf{BC\ (\mu g\ m^{-3}) = (0.27 \pm 0.03) * BSI_{(British)} - (4.0 \pm 0.2) * 10^{-4}\ BSI_{(British)}^{2}}$$

**Equation 5.3**

# Aims of this chapter

As part of this project a method for retrospectively determining equivalent black carbon or elemental carbon concentrations would be expected to provide insights into traffic emissions in London. The black smoke to black carbon equation provided by Heal and Quincey (2012) is one such method but the derived concentrations would not be directly related to a $PM_{10}$ or $PM_{2.5}$ measurement.

Based on the work of Heal and Quincey (2012) and the studies reported above it is also likely that a method for determining the light attenuation from time-resolved filters based on either transmissometry or reflectometry could provide surrogate carbon measurements. Chow et al. (2010) point out that additional useful information on "light-absorbing carbon or black carbon content" can be obtained from Teflon-membrane filters used to determine compliance with regulatory requirements and these data would enhance the "ability to establish relationships" among ambient PM concentrations and, inter alia, health effects.

As previously discussed in the UK quartz fibre filters were originally used as the filter substrate for gravimetric measurements made by the Partisol 2025 method but this changed nationally in 2007 to Emfab™, which consists of borosilicate microfibres reinforced with woven glass cloth and bonded with PTFE ('Teflon') (www.pall.com/lab). The change was recommended in a report by Bureau Veritas HS&E Ltd (2008) because "Emfab filters appear to be less influenced by artefacts than quartz filters." Therefore a method for determining light absorbing carbon concentrations of PM mass collected using, for example, a Partisol sampler on both quartz fibre and Emfab™ filter substrates would be expected to provide concentrations relating to traffic emissions not only extending back in time but also broadening the area where concentrations might be determined at a relatively small financial cost. Such measurements would also be of use in health studies, both current and retrospective.

In order to provide some quantification of traffic emissions in London both retrospectively and for sites where PM mass measurements might be available but not any other particulate carbon measurement (e.g. Oxford Street) it was decided to seek an equation for light absorbing carbon of PM mass collected on time-resolved filter samples where either quartz fibre or Emfab$^{TM}$ is the substrate. Currently no equation is known to be available for Emfab$^{TM}$ filters and only project specific equations such as those described above in respect of quartz fibre filters. Reflectometer and transmissometer instruments were available for this research project and have been employed as described in chapter 2.

Magee Scientific developed the Sootscan Model OT21 Transmissometer as a laboratory based instrument as described in chapter 2 based on the same principles as the real-time aethalometers (Magee Scientific, 2010). The transmissometer provides a measure of attenuation (ATN) in the same way as the aethalometer described above. Magee Scientific in their Product Specifications (www.mageescientific.com) report that 1 ATN unit represents a BC concentration of 0.14 μg $m^{-3}$ (Magee Scientific 2010). However no correction is made, or indeed suggested, for any loading effect in line with Virkkula et al.'s (2007) loading effect correction.

It was decided to seek relationships empirically between reflectometer (R) and transmissometer (ATN) measurements and collocated EC measurements.

As part of this project, reflectometer measurements were made on one hundred (100) of the fine filters collected during 2001 and 2002 at Acton Town Hall and the filters subsequently sent for analysis by the IMPROVE-TOR method at the Desert Research Institute in the US (see chapter 2 for details). No transmissometer measurements are available for these filters. Transmissometer measurements were however made (as part of different research projects – see Sweeney (2008) and Tremper et al. (2013)), on 103 quartz filters collected at North Kensington and Marylebone Road during 2003 to 2005 and 2010. Those filters were subsequently analysed by the NIOSH-TOT method to determine the elemental carbon concentration on each filter. It is important to note that the elemental carbon analysis was carried out by two different thermal-optical methods. Unfortunately there were no elemental carbon measurements, made by either thermal optical method, of quartz filters where both reflectometer and transmissometer measurements were available.

Reflectometer (R) and transmissometer (ATN) measurements were determined, as part of this research project, using Emfab™ PM10 filters collected using a Partisol 2025 sampler at Marylebone Road between January 2010 and May 2012. On 548 of those days co-located daily elemental carbon measurements derived by the NIOSH TOT method from quartz fibre filters collected with a Partisol 2025 sampler were also available. Details of the IMPROVE-TOR and NIOSH-TOT methods are set out in chapter 2.

Details of the filters available for this part of the analysis are set out in Table 5.1.

*Table 5.1 Summary of data used for comparison with light attenuation and collocated elemental carbon measurements.*

| Study site | Gravimetric measurement filter substrate | Sampling Period | EC analysis method | Light attenuation measurement method | n |
|---|---|---|---|---|---|
| Acton Town Hall | Quartz fibre | 2001 – 2002 | IMPROVE-TOR | Reflectometer | 100 |
| North Kensington and Marylebone Road | Quartz fibre | 2003 – 2005 and 2010 | NIOSH-TOT | Transmissometer | 103 |
| Marylebone Road | Emfab™ | 2010 – 2012 | NIOSH-TOT | Reflectometer and Transmissometer | 548 |

The measurements obtained from the reflectometer (R) are expressed in percentage values between 1 – 100, where 100 represents a blank, unloaded, filter. These measurements were converted to **ln Ro/R** (where Ro = the intensity of reflected light from the surface of a clean paper; and R = the intensity of reflected light from the surface of a stained paper.).

As discussed in chapter 2, the transmissometer returns attenuation (ATN) values at both infrared (λ = 880nm) and ultraviolet (λ = 320nm) wavelengths. The infrared values were expected to correspond most closely to atmospheric carbon from incomplete combustion and have been used here. 1 ATN unit is the equivalent of ln Io/I *100. The ATN (IR) units were therefore converted to **ln Io/I** by dividing the returned ATN value by 100.

As previously discussed, both measurements, (ln Ro/R) and (ln Io/I), are based on the principles of the Beer-Lambert Law.

# Relationship between transmissometer and reflectometer measurements

There are two principal differences between reflectance and transmittance measurements of light absorbing particles on a filter:

Firstly the light source is different. In reflectometry a broadband light is used whereas in transmissometry measurements different light wavelengths may be used. As previously discussed the infrared transmittance measurements ($\lambda$ = 880 nm) have been used in this study.

Secondly in transmission there is one single pass of light at a predetermined wavelength through the filter where the relationship between intensity of light measured before (Io) and after (I) provides an attenuation coefficient. The theory of reflectance measurement is somewhat more complicated and is explained in Annex A of ISO 9835 (1993) which dealt with determining a black smoke index using reflectometry. In summary, in the first instance it is assumed that the filter substrate acts as a 'perfect mirror' and hence 'radiation passes through the absorbing layer (ie the particles on the top of the filter) twice'. Therefore Lambert's Law could be adapted for reflectance measurements from a filter substrate by using the following equation:

$$a = (A/2V) \times \ln(Ro/R) \qquad \text{Equation 5.4}$$

Where $a$ = the absorption coefficient, in reciprocal metres, A = the area of the stain, in square metres, and V = the volume of air sampled, in cubic metres.

However, it is also pointed out in ISO 9835 that this equation may only be used in 'an ideal situation' which only exists when monochromatic light is used and the particulate material collects on the surface of the filter. Black smoke measurements were traditionally made using Whatman No 1 filter paper and this was in essence acknowledged not to represent the ideal situation because, inter alia, the particles penetrate into the paper and therefore the above equation was considered to approximate to

$$a_1 = (A/V) \times \ln(Ro/R) \qquad \text{Equation 5.5}$$

Essentially a factor of 2 was introduced into the equation (5.4 above) to provide for the double passage of light through the filter in reflectometry and then removed as using Whatman No 1 filter paper was deemed not to be "the ideal situation". Therefore the calibration curve in Figure A1 of ISO 9835 and calculations in Table A.1 provide an absorption coefficient measurement *(a)* as set out in equation 5.4 above and to provide an appropriate measurement for Whatman No 1 filters this figure needed to be multiplied by 2 to achieve the revised absorption coefficient ($a_1$) as set out in Equation 5.5 above.

The scatterplot relationships between the reflectometer and transmissometer measurements carried out on each filter are demonstrated in Figures 5.1 and 5.2. For clarity, this comparison has been carried out on all filters measured by both reflectometry and transmissometry and therefore filters obtained from the Oxford Street sampler have been included here. A summary of the filters used is set out in Table 5.2. It should also be noted that in this analysis the sampling period was determined by filter availability and no other reason.

*Table 5.2 Details of filters analysed by both reflectometry and transmissometry*

| Site | Sampling period | n |
|---|---|---|
| **Quartz fibre filters** | | |
| Acton Town Hall | 2001 – 2002 | 273 |
| North Kensington | 2003 – 2005 | 115 |
| Marylebone Road | 2003 – 2005 | 157 |
| **Emfab™ filters** | | |
| Marylebone Road | January 2010 to 5 June 2012 | 614 |
| Oxford Street | January 2011 to 31 July 2012 | 540 |

*Figure 5.1 Scatterplot demonstrating relationship between reflectometry and transmissometry measurements carried out on quartz fibre filters 2001 – 2005.*

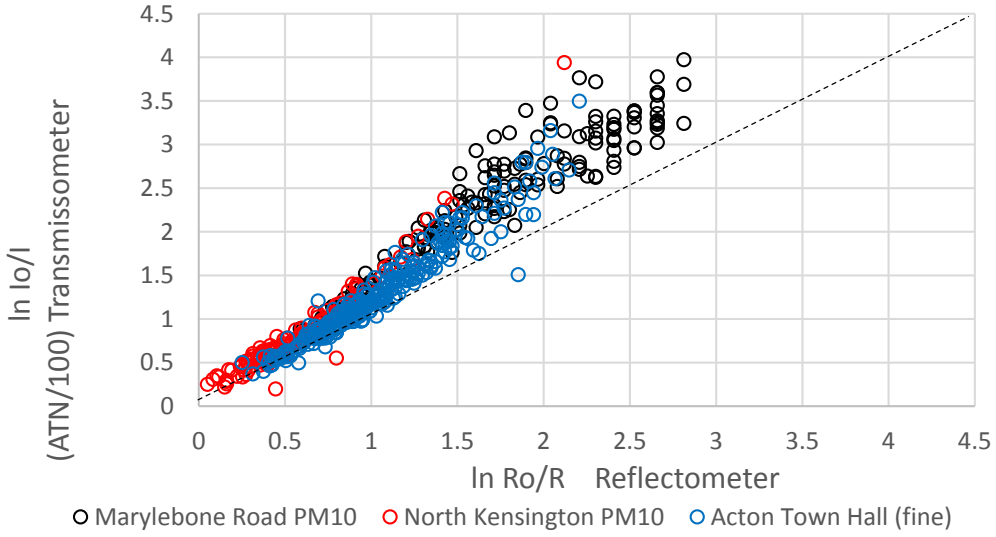
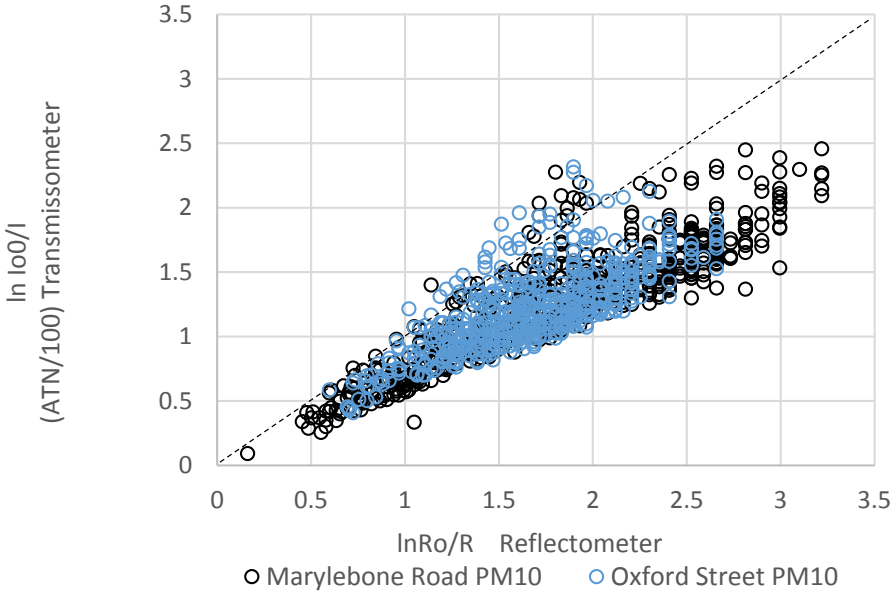



*Figure 5.2 Scatterplot demonstrating relationship between reflectometry and transmissometry measurements carried out on Emfab™ filters 2010 – 2012.*



It is interesting to note that, whilst there are clear relationships between the measurements on each filter substrate there are also clear differences between the filter types. The 1:1 line has been drawn on each chart to demonstrate these differences. Table 5.3 sets out the reduced major axis regression analysis comparing the relationships between the measurements

Table 5.3 *Reduced Major Axis relationships between reflectometer and transmissometer measurements made at each site*

| Site | Sampling period | n | r | Gradient | Intercept | Mean ln Io/I | Mean lnRo/R |
|---|---|---|---|---|---|---|---|
| **Quartz filters** | | | | | | | |
| Acton Town Hall | 2001 – 2002 | 273 | 0.97 | 1.4±0.02 | -0.2±0.02 | 1.2 | 1.0 |
| North Kensington | 2003 – 2005 | 115 | 0.96 | 1.6±0.04 | -0.06±0.02 | 0.8 | 0.6 |
| Marylebone Road | 2003 – 2005 | 157 | 0.94 | 1.3± 0.03 | 0.2± 0.06 | 2.4 | 1.8 |
| **Emfab™ filters** | | | | | | | |
| Marylebone Road | 2010 - 2012 | 614 | 0.89 | 0.7±0.01 | 0 | 1.3 | 1.8 |
| Oxford Street | 2011 - 2012 | 540 | 0.74 | 0.8±0.02 | -0.07±0.03 | 1.2 | 1.7 |

The quartz fibre filters absorption coefficient derived from the reflectometer measurements is less than the equivalent transmissometer measurement. By contrast the absorption coefficient derived from the reflectometer measurements is greater than its equivalent transmissometer measurement on the Emfab™ filters. These differences may, at least partially, be as a result of different multiple light scattering from the different filter substrates having a greater influence on the reflectance measurements. It is not possible from this analysis however to be clear how each of these filters may diverge from the "ideal situation" referred to in ISO 9835 as discussed above. Hammonds (2012) determined empirically that the value of 2 was too high for quartz filters and considered that a factor of 1.2 would be more appropriate.

Edwards et al. (1983) also reported different relationships between transmittance and reflectance depending on filter substrate (including quartz fibre). They suggested that the "optical effect of the penetration of particles into a porous filter is less amenable to

analytical treatment because of the unknown (and probably variable) depth of penetration as well as multiple scatter effects within the filter." The review articles of both Moosmüller et al. (2009) and Giechaskiel et al. (2014) indicate that filter based absorption is "strongly influenced" by filter type and its specific characteristics. It was also clear that filter substrate was an important consideration when deciding on monitoring methods as evidenced by the change from quartz fibre to Emfab™.

It was decided therefore that different calibrations for different filter substrates and measurement method will need to be determined and compared to achieve the aims in this research project.

# Comparison of measured EC concentrations against reflectometer and transmissometer measurements.

In this section reflectometer and transmissometer measurements are compared against collocated EC concentrations (details in Table 5. 1 above), as follows:

| | |
|---|---|
| **QUARTZ FIBRE FILTERS** | Acton Town Hall (2001 – 2002),<br>North Kensington and Marylebone Road (2003 – 2005)<br>North Kensington and Marylebone Road (2010) |
| **EMFAB™ FILTERS** | Marylebone Road (2010 – 2012) |

As EC concentrations have been derived by two different methods the following nomenclature is used in this section to distinguish the measurement method:

EC (IMPROVE-TOR) ($\mu g\ m^{-3}$) (Acton Town Hall only)

EC (NIOSH-TOT) ($\mu g\ m^{-3}$) (North Kensington and Marylebone Road)

Details of these methods, together with a summary of their similarities and differences, are given in chapter 2.

# Quartz fibre filters

## REFLECTOMETER

The scatterplot relationship between elemental carbon measured on 100 of the fine filters collected at Acton Town Hall (2001 – 2002) and its corresponding reflectometer measurements is demonstrated in Figure 5.3. The straight line relationship is given by

$$\mathbf{EC\ (IMPROVE\text{-}TOR)(\mu g\ m^{-3})\ = 3.96 \pm 0.2\ (\ln(Ro/R))} \qquad \mathbf{r^2\ 0.8}$$

**Equation 5.6**

Whilst there is clearly a strong correlation between these measurements, it is also clear that the relationship is not best described by a straight line relationship and this is undoubtedly an indication of scattering and shadowing on the filter, as described above. The best fit quadratic relationship in the variable lnRo/R is given by

$$\mathbf{EC\ (IMPROVE\text{-}TOR)\ (\mu g\ m^{-3}) = 1.785 \pm 0.2\ ((\ln(Ro/R))^2) + 1.5332 \pm 0.3\ (\ln(Ro/R))} \qquad \mathbf{r^2\ 0.95}$$

**Equation 5.7**

No transmissometer measurements were made using these filters.

## TRANSMISSOMETER

As previously noted transmissometer measurements were also available as part of different research projects (see Sweeney, 2008 and Tremper et al., 2013). A sample of PM10 filters (quartz fibre) from Marylebone Road and North Kensington obtained between 2003 and 2005 and during 2010 (n = 103) have both transmissometer and elemental carbon (IMPROVE-TOT) measurements (but no reflectometer measurements). Although they have been collected at two different locations in central London the results have been combined to provide the best representative sample possible.

Figure 5.4 is the scatterplot of this relationship. There is a considerable time gap (2005 – 2010) between the filter samples available from Marylebone Road. However, the 2010 data fall within the same range as the earlier data and is therefore considered to be equally representative of black carbon in the quartz filter samples.

In this instance, the straight line relationship is given by:

**EC (NIOSH-TOT) ($\mu g\ m^{-3}$) = 2.75 ±0.2 (ln (Io/I))** **$r^2$ 0.83**

**Equation 5.8**

where ln (Io/I) = ATN IR/100

Again, there is a strong correlation between the two measurements but it is not a straight line relationship. The best fit quadratic relationship in the variable ln Io/I is given by:

**EC (NIOSH-TOT) ($\mu g\ m^{-3}$) = 0.8605±0.1 $((\ln(Io/I))^2)$ + 0.7382 ± 0.3 (ln(Io/I))**

**$r^2$ 0.93**

**Equation 5.9**

where ln (Io/I) = ATN IR/100

*Figure 5.3 Scatterplot of the relationship between EC (IMPROVE-TOR) concentrations and ln Ro/R with straight line and quadratic relationships best fit trendlines, Acton Town Hall 2001 – 2002 (n = 100)*

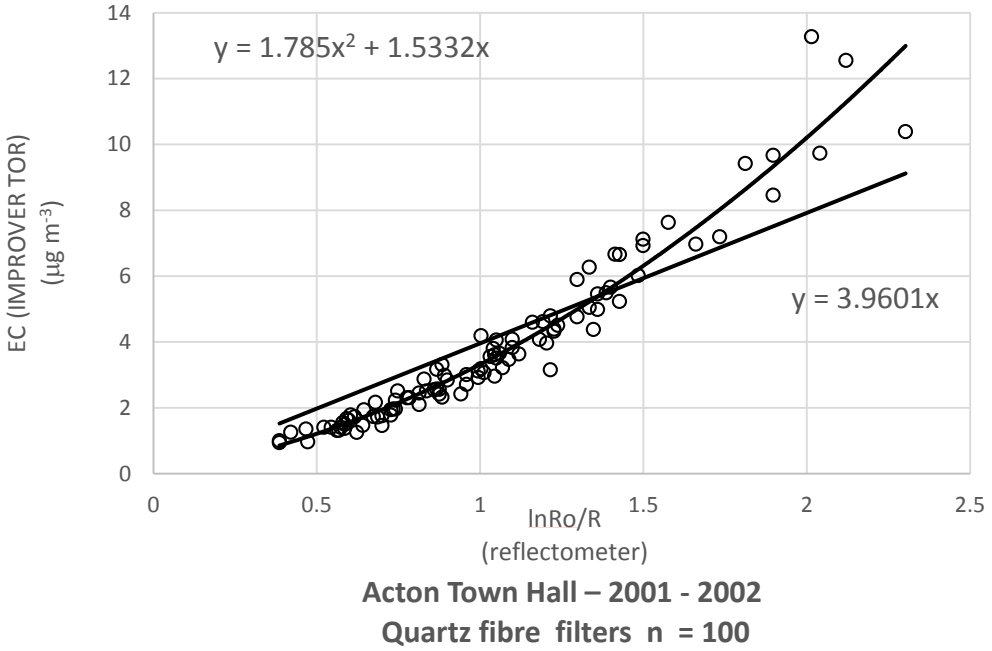
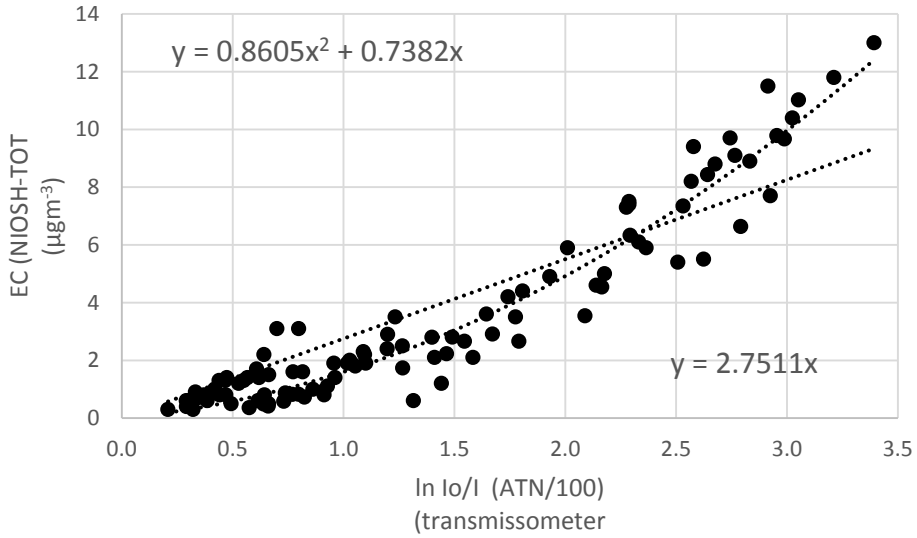



*Figure 5.4 Scatterplot of the relationship between EC (NIOSH-TOT) concentrations and ln Io/I with straight line and quadratic relationships best fit trendlines, Marylebone Road and North Kensington 2003 – 2005 and 2010 (n = 103 )*



# Emfab filters (2010 – 2012)

It was easier to compare both reflectometer and transmissometer measurements made on the same Emfab$^{TM}$ filters collected at Marylebone Road during 2010 to 2012 with carbon measurements because there were also daily co-located elemental carbon concentration measurements (μg $m^{-3}$) in PM10 mass determined using the NIOSH-TOT method. The results are set out below. It should be noted that daily co-located black carbon measurements determined using a Magee aethalometer (AE22) were also available and could have been used to provide this calibration. However it was decided that it would be more useful to calibrate all measurements across all the datasets with similar measurement techniques and therefore only the EC concentrations have been used.

## REFLECTOMETER

The scatterplot relationship between the NIOSH-TOT elemental carbon on 548 days between 2010 and 2012 at Marylebone Road and the same day reflectometer measurements is demonstrated in Figure 5.5(a). The straight line relationship is given by

**EC (NIOSH-TOT) (μg $m^{-3}$) = 3.8322±0.05 (ln(Ro/R))** **$r^2$ 0.80**

**Equation 5.10**

The best fit quadratic relationship in the variable lnRo/R is given by

**EC (NIOSH-TOT) (μg $m^{-3}$) = 0.7707±0.1 (( ln(Ro/R))$^2$) + 2.1082± 0.3(ln(Ro/R))**

**$r^2$ 0.85**

**Equation 5.11**

.

## TRANSMISSOMETER

The scatterplot relationship between the NIOSH-TOT elemental carbon on 548 days between 2010 and 2012 at Marylebone Road and transmissometer measurements is demonstrated in Figure 5.5(b). The straight line relationship is given by

**EC (NIOSH-TOT) ($\mu g\ m^{-3}$) = 5.396 ± 0.1(ln(Io/I))** **$r^2$ 0.64**

**Equation 5.12**

The best fit quadratic relationship in the variable lnIo/I is given by

**EC (NIOSH-TOT) ($\mu g\ m^{-3}$) = 0.3596±0.3 $((\ln(Io/I))^2)$ + 4.8311 ± 0.5 (ln(Io/I))**

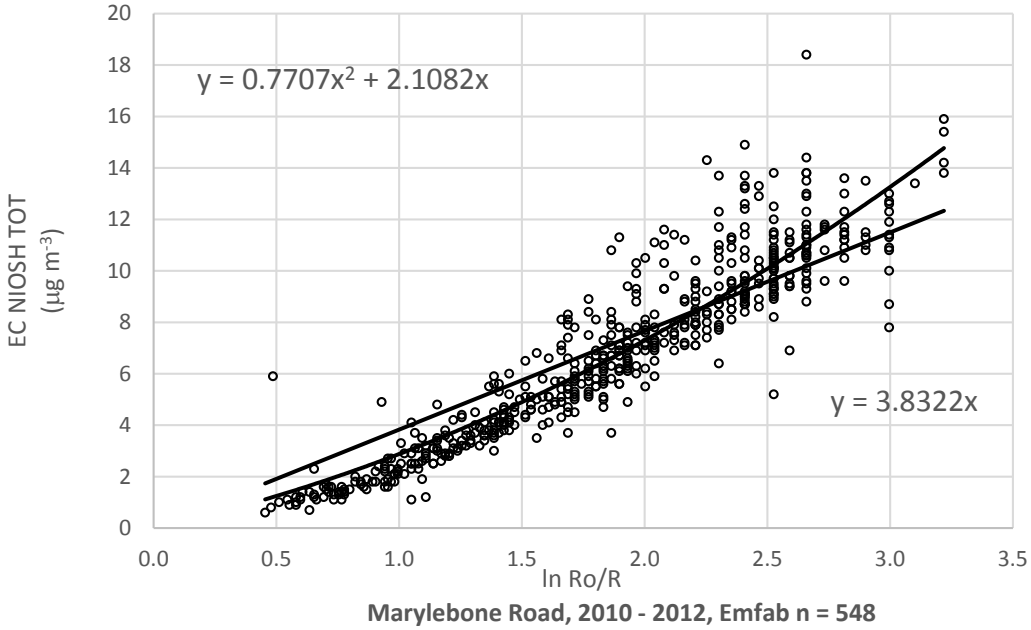
**$r^2$ 0.65**

**Equation 5.13**

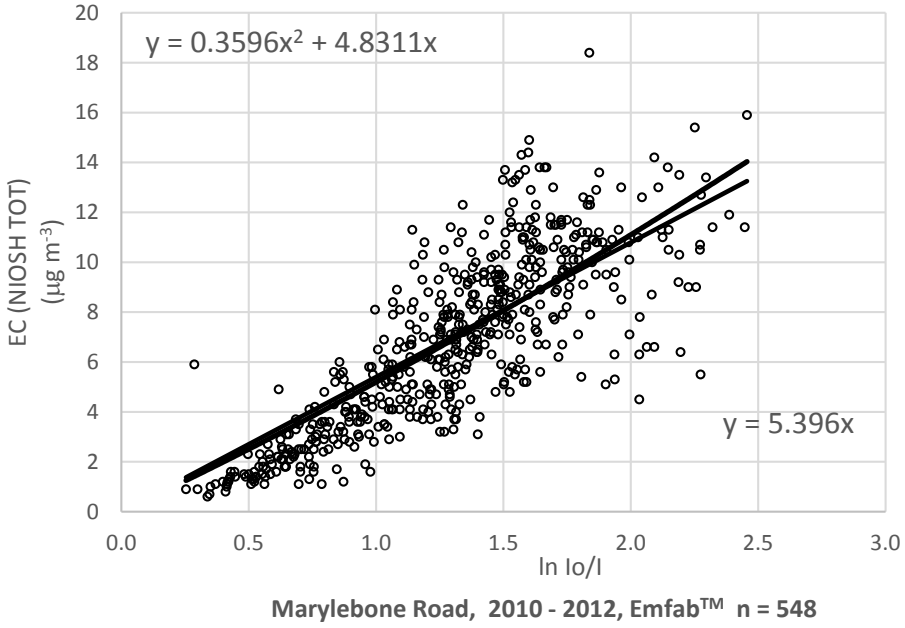
There is noticeable variation in scatter in the data between the different filter substrates demonstrated in Figures 5.3 - 5.5. The elemental carbon concentrations used for the calibration from the quartz filters were directly derived from the filter used to determine light absorption (both methods). By contrast, Emfab filters are not suitable for thermal optical analysis for elemental carbon and collocated EC concentrations derived from quartz filters were used introducing another level of uncertainty.

*Figure 5.5 Scatterplot of the relationship between EC (NIOSH-TOT) concentrations, Marylebone Road, 2010 – 2012, Emfab™ filters, n = 548*

*(a) ln Ro/R (reflectometer) with straight line and quadratic relationships best fit trendlines*




*and, (b) ln Io/I (transmissometer) with straight line and quadratic relationships best fit trendlines*



# Associated uncertainty of determined quadratic equations

To summarise, the linear and quadratic equations determined in the previous section (with the 95% confidence intervals for each coefficient) are set out in Table 5.4.

*Table 5.4 Summary of linear and quadratic regression analysis for reflectance/transmission against elemental carbon concentrations*

| | **Linear relationship with EC (±95% CI)** | **Quadratic relationship with EC (±95% CI)** |
|---|---|---|
| **Quartz** | | |
| **Reflectance** | 3.96± 0.2 ln (Ro/R) | 1.785±0.2 (ln(Ro/R)$^2$) + 1.5332±0 .3 ln (Ro/R) |
| **Transmittance** | 2.75 ± 0.2 ln (Io/I) | 0.8605 ±0.1 (ln(Io/I)$^2$) + 0.7382 ±0.3 ln (Ro/R) |
| **Emfab™** | | |
| **Reflectance** | 3.8322± 0.05 ln (Ro/R) | 0.7707±0.1 (ln(Ro/R)$^2$) + 2.1082 ±0 .3 ln (Ro/R) |
| **Transmittance** | 5.396 ± 0.1 ln (Io/I) | 0.3596 ±0.3 (ln(Io/I)$^2$) + 4.8311 ± 0.5 1ln (Ro/R) |

The quadratic equations determined empirically in this study as set out in Table 5.4 represent the best fit lines in each case and are also similar in form to those described by, for example, Bailey and Clayton (1982), Virkkula (2007) and Heal and Quincey (2012), *inter alia*. The equations are therefore expected to include a correction factor for loading/light scattering etc. and provide useful conversion factors for measurements derived using either a reflectometer or transmissometer. It should be noted that these equations may be applied across the whole range of possible reflectance (5 %R – 95%R) and transmittance (40 – 400 ATN units) measurements.

The uncertainty associated with these equations has been calculated using the Guide to the expression of uncertainty in measurement (GUM) (ISO, 1995). GUM states that the combined standard uncertainty involves combining the individual uncertainty components as variances, i.e. root sum squares, with sensitivity functions from partial derivatives of the measurement equation with respect to each individual uncertainty, i.e.:

$$Uc^z = \sum_{1=1}^{n} \left[ \left( \frac{df}{dx_1} \right) Ucx_1 \right]^2$$

*Combined uncertainty* *partial derivative* *uncertainty in each component* $x_1$

The quadratic equations in Table 5.4 take the general form:

$$EBC = ax^2 + bx$$

$$where\ x = either \ln\left(\frac{Io}{I}\right) or \ln\left(\frac{Ro}{R}\right)$$

So:

$$U(EBC) = \sqrt{[U(a)x^2]^2 + [U(b)x]^2 + [U(x)(2ax + b)]^2}$$

*where*

$U(a) = uncertainty\ associated\ with\ the\ quadratic\ coefficient\ (a)$

$U(b) = uncertainty\ associated\ with\ the\ linear\ coefficient\ (b)$

$x = the\ arithmetic\ mean\ of\ either \ln\left(\frac{Io}{I}\right) or \ln\left(\frac{Ro}{R}\right)$

$U(x) = uncertainty\ associated\ with\ x$

The uncertainty associated in respect of the quartz filters is 40% based on the reflectance measurements and 50% based on the transmission measurements and the uncertainty associated with the Emfab filters is 35% based on the reflectance measurements and 53% based on the transmission measurements. The uncertainty determined by this method was therefore similar between filter substrates and light absorption measurement methods.

## Mass extinction coefficients and loading correction factors

The regression equations determined in this study (summarised in Table 5.4 above) can also yield comparative information regarding mass extinction coefficients ($\sigma_{ATN}$) and loading/shadowing/ scattering correction factors ($k$) for each filter type and measurement method which may in turn quantify the particle and filter substrate interactions and help in deciding which equation would be most suitable for use in quantifying EBC concentrations.

In the first instance, the mass extinction coefficient ($\sigma_{ATN}$) may be empirically derived as set out by Chow et al. (2012) and Heal and Quincey (2012). The gradient of the linear regression of the plot of elemental carbon against either ln (Ro/R) or ln (Io/I) as appropriate, yields $A*10^6/V*\sigma_{ATN}$ (where A is the area of the exposed part of a filter and V is the volume of air sampled). The area of the exposed part of a Partisol filter was $0.0011946m^2$ and the volume of air sampled in 24 hours through a Partisol sampler was $\sim 24m^3$. As Heal and Quincey (2012) point out this would however only represent the simplified case where k= 0 (i.e. there is no loading or scattering effect) and it is clear from Figures 5.3 - 5.5 that the relationships are not best described by a straight line and $k$ does not =0. Heal and Quincey (2012) go on to point out that the linear coefficient of a quadratic equation with the same variables might also be expected to yield a value for $\sigma_{ATN}$.

Table 5.5 compares the range of $\sigma_{ATN}$ calculated using the gradient of the linear slope (i.e. assuming that k = 0) and its 95% confidence limits of each filter type and measurement method with the corresponding linear coefficient reported in the quadratic equations. For the purposes of this calculation both types of filter in this study are assumed to be analogous

to Whatman No 1 and therefore "the ideal situation" referred to in ISO 9835 (1992) would not arise and the modified calculation set out in Annex A of the Standard as reported above should be used (i.e. no factor of 2 is introduced when considering the results obtained using the reflectance method for either filter substrate).

*Table 5.5 Range of mass extinction coefficients (σATN) determined for each regression analysis (linear and quadratic) with EC*

| | **95% CI for σATN ($m^2 g^{-1}$) assuming k = 0 based on gradient derived in Equations 5.6, 5.8, 5.10, and 5.12** | **95% CI for σATN ($m^2 g^{-1}$) based on linear coefficient of relevant quadratic best line fit in Equations 5.7, 5.9, 5.11 and 5.13 -** |
|---|---|---|
| **Quartz** | | |
| **Reflectance** | 12.0 – 13.2 | 27.2 – 40.3 |
| **Transmittance** | 16.9 – 19.5 | 48.0 – 113.6 |
| **Emfab™** | | |
| **Reflectance** | 12.8 – 13.2 | 20.7 – 27.5 |
| **Transmittance** | 9.1 – 9.4 | 9.4 – 11.5 |

Unlike the relationships found by Heal and Quincey (2012) there are distinct differences between the linear coefficients of each equation of the straight line and the quadratic equation and these differences have produced a large range of possible mass extinction coefficients. Weingartner (2003) cited a range of studies reporting mass extinction coefficients ranging from 5 $m^2 g^{-1}$ in remote areas, 14 $m^2 g^{-1}$ at urban locations and 20 $m^2 g^{-1}$at "near-street measuring sites". In their review paper, Bond and Bergstrom (2006) report mass absorption cross sections ((ie $\sigma_{ATN}$ ) ranging between 3 and 30 $m^2 g^{-1}$ (λ 550nm) and suggest that a value of 7.5± 1.2 $m^2 g^{-1}$ (λ 550nm) is an appropriate coefficient for freshly emitted light absorbing carbon. Chow et al. (2010) report a mass extinction coefficient of 11.1 $m^2 g^{-1}$ across the entire IMPROVE network in the US during 2005 – 2006 (n = 32,372). The mass extinction coefficients reported for the Emfab filters fall within similar ranges to these studies, particularly when considering the transmission coefficients. The reflectance mass extinction coefficients may be influenced by the factor of 2 referred to above and may be up to 50% less than those reported. The mass extinction coefficients for the quartz filters demonstrate a considerable range based on these methods. As the filter becomes loaded the properties of the filter substrate together with loading factors, for example the way in which particles collect on and potentially within the filter matrix, make it difficult to derive a mass extinction coefficient based on a polynomial relationship between the

variables. Any comparisons between mass extinction coefficients based on different filter substrates and measurement methods should therefore be treated with some caution.

Heal and Quincy (2012) go on to state that a value for the correction factor (k) may be determined by dividing the quadratic coefficient by the linear coefficient determined in the quadratic equations. In their study Heal and Quincey (2012) determined a value of 0.77 which related to black smoke reflectance measurements from Whatman No 1 filters. The range of loading correction factors, taking into account the 95% confidence intervals, derived using this method in this study are set out in Table 5.6. As may be seen the correction factors fall either side of the factor determined by Heal and Quincey (2012) and differ according to filter substrate. The loading correction factors for the quartz filters were similar by either measurement method whilst there was a greater difference between the measurement methods when considering Emfab filters, but with very little correction for loading being apparent by either method for this type of filter.

*Table 5.6 Range of loading correction factors (k) determined using the relationship between the quadratic and linear coefficients of the polynomial regression analysis, light absorption against elemental carbon.*

| | **95% CI for loading correction (k) based on relationship between quadratic and linear coefficients in Equations 5.7, 5.9, 5.11 and 5.13** |
|---|---|
| **Quartz** | |
| **Reflectance** | 1.1 – 1.3 |
| **Transmittance** | 0.9 – 1.7 |
| **Emfab™** | |
| **Reflectance** | 0.4 |
| **Transmittance** | 0.01 – 0.1 |

It is interesting to note that the shadowing correction factors for the quartz filters remain similar even though the reflectance measurements were from samples obtained in 2001 and 2002 and the transmittance measurements span a timescale from 2003 to 2010, suggesting that the particle mix has not altered significantly over that period of time.

In conclusion, filter substrate and the method measuring light absorption, ie the contrast between broadband, reflected, light and one single transmission of light in the infrared wavelength, is influential when considering both mass extinction coefficients and loading correction factors.

# Reflectometer versus Transmissometer: application of equations from each instrument to daily measurements

In this section the quadratic equations determined above are applied to the datasets described in Tables 5.1 and 5.2 above. Petzold et al. (2013) point out there is no agreement on the terminology that considers all aspects of the specific properties of "black carbon". The terms black carbon, elemental carbon and black smoke are all defined by their measurement method and within each category there are different analysis methods and interpretations thereof. Petzold et al. (2013) provide historic definitions of these species, pointing out that the first definition of 'black carbon' was made by Gundel et al. (1984), together with current terminology. They suggested that for quantitative applications, such as reporting data from observations, more specific terminology should be used. They strongly recommend that "BC" should be avoided to describe evolved carbon methods and that equivalent Black Carbon ("EBC") "should be used instead of black carbon for data derived from optical absorption methods, together with a suitable MAC for the conversion of light absorption coefficient into mass concentration". Here the mass extinction coefficient was referred to as "MAC".

In line with Petzold et al.'s (2013) recommendations EBC has been used to define the species measured as the concentrations have been "derived from optical absorption methods" and for the avoidance of doubt, the following expressions have been used to describe the concentrations derived from the equations determined in the previous section:

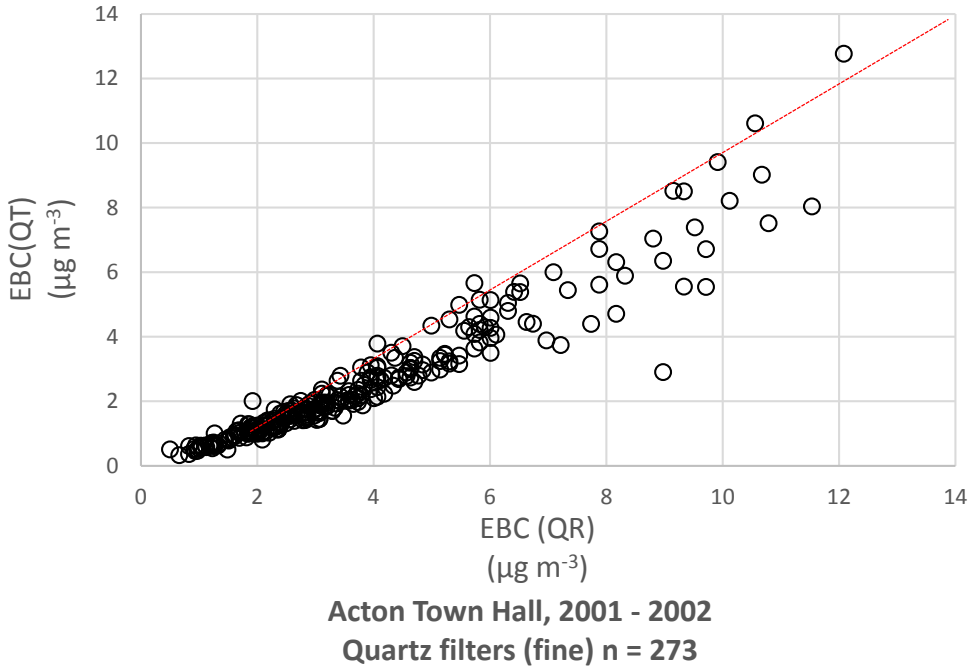
| **EXPRESSION:** | **REFERS TO CONCENTRATIONS DETERMINED BY:** |
|---|---|
| **EBC (QR)** | Equation 5.7 namely, $1.785((\ln(Ro/R))^2) + 1.5332\ (\ln(Ro/R))$ (Quartz fibre filters, reflectometry, EC (IMPROVE-TOR) |
| | |
| **EBC (QT)** | Equation 5.9 namely, $0.8605((\ln(Io/I))^2) + 0.7382(\ln(Io/I))$ (Quartz fibre filters, transmissometry, EC NIOSH-TOT) |
| | |
| **EBC (ER)** | Equation 5.11 namely, $0.7707((\ln(Ro/R))^2) + 2.1082\ (\ln(Ro/R))$ (Emfab™ filters, reflectometry, EC NIOSH-TOT) |
| | |
| **EBC (ET)** | Equation 5.13 namely, $0.3596((\ln(Io/I))^2) + 4.8311\ (\ln(Io/I))$ (Emfab™ filters, transmissometry, EC NIOSH-TOT) |

Figures 5.6(a), (b), (c) and (d) are the scatterplots comparing the results of applying the equations determined in the previous section, in respect of both reflectometer and transmissometer measurements, to the following datasets in order to determine EBC concentrations:

| | | |
|---|---|---|
| Acton Town Hall | 2001 – 2002 | n = 273 (quartz fibre filters) |
| Marylebone Road | 2003 – 2005 | n = 157 (quartz fibre filters) |
| North Kensington | 2003 – 2005 | n = 115 (quartz fibre filters) |
| Marylebone Road | 2010 – 2012 | n = 583 (Emfab$^{TM}$ filters) |

*Figures 5.6* *Scatterplot relationships between EBC derived from transmissometer measurements and EBC derived from reflectometer measurements at*

*(a) Acton Town Hall 2001 - 2002*




*(b) Marylebone Road 2003 - 2005*

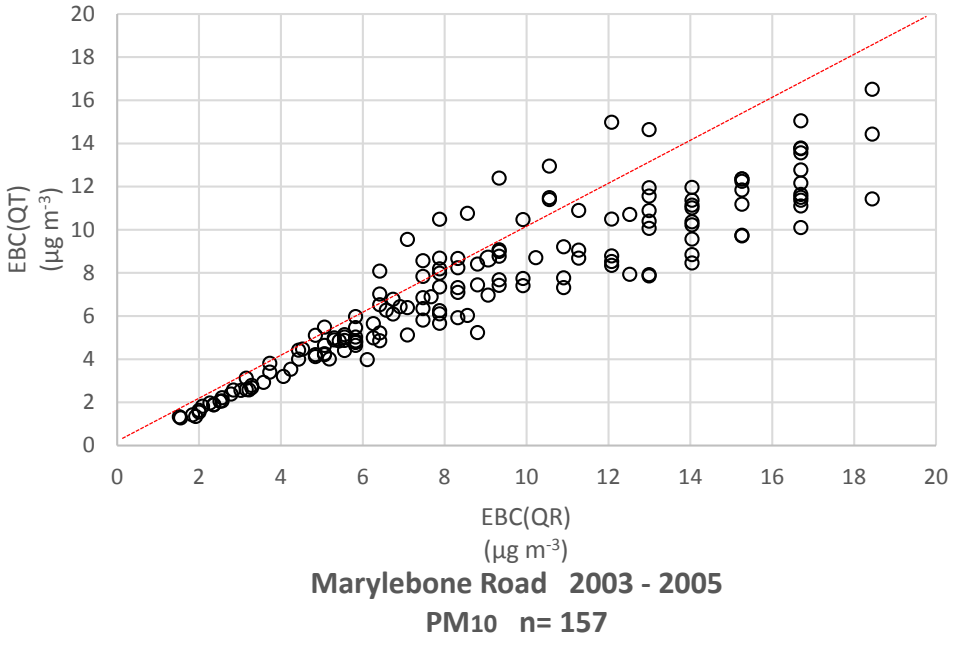
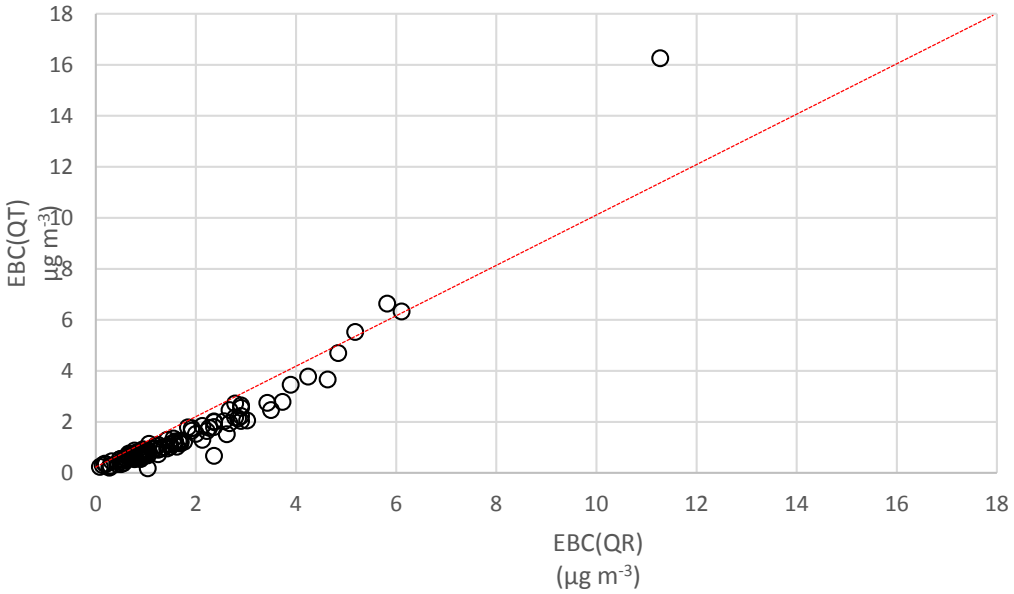


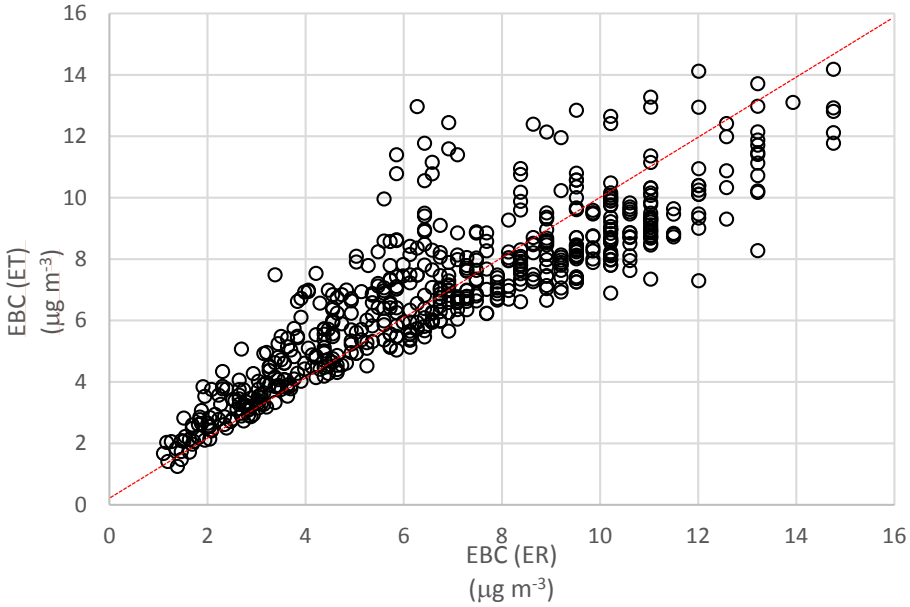
*Figure 5.6 (continued)* *Scatterplot relationships between EBC derived from transmissometer measurements and EBC derived from reflectometer measurements at*

*(c) North Kensington 2003 - 2005*




**North Kensington 2003 - 2005**
**PM10 n = 115**

*(d) Marylebone Road 2010 - 2012*




**Marylebone Road 2010 - 2012 n = 583**

Table 5.7 sets out the reduced major axis relationships between the concentrations derived from these calculations. In each case the transmissometer derived concentrations (EBC (QT) and EBC (ET)) are on the y axis.

*Table 5. 7 Reduced Major Axis relationships between EBC derived from transmissometer measurements and EBC derived from reflectometer measurements*

| Site | Sampling period | n | r | Gradient | Intercept |
|---|---|---|---|---|---|
| **Quartz filters** | | | | | |
| Acton Town Hall | 2001 – 2002 | 273 | 0.95 | 0.85±0.02 | -0.7±0.07 |
| North Kensington | 2003 – 2005 | 115 | 0.95 | 1.2±0.03 | -0.6±0.08 |
| Marylebone Road | 2003 – 2005 | 157 | 0.92 | 0.78±0.03 | -0.5±0.3 |
| **Emfab filters** | | | | | |
| Marylebone Road | 2010 - 2012 | 583 | 0.87 | 0.82±0.02 | 1.3±0.13 |

It is clear that there is significant correlation between the two types of measurements but it would seem that at two of the locations, namely Acton Town Hall and Marylebone Road, the transmissometer method predicted between 15% to 22% less EBC (both filter substrate types) whilst at North Kensington the transmissometer method over-predicted by about 20%. However there is one outlier which is recorded in both datasets at North Kensington. This occurred on Sunday 20 November 2005 when a daily mean PM10 concentration of 92.5 μg $m^{-3}$ was also recorded. An inspection of the co-located TEOM records suggest that this high concentration related to a short-lived event in the early hours of the morning but no record of the event itself has been logged. If this outlier is removed from the RMA calculations then a gradient of 0.95±0.02 is derived with an intercept of –0.2±0.05 and an r value of 0.96. This expression is then more similar to the ones derived at the other sites.

Table 5.8 sets out the mean (arithmetic), minimum and maximum concentrations derived from each equation for comparison. As in the scatterplots (Figure 5.6) the concentrations derived from the quartz fibre, reflectometer measurements (EBC (QR)) are higher than the comparable transmissometer measurements. EBC (QR) was determined based on a calibration with EC calculated using the IMPROVE-TOR protocol in contrast to EBC (QT) which was calibrated against EC derived by the NIOSH-TOT method. Chow et al. (2001) compared the two protocols (IMPROVE/ NIOSH) and concluded that, whilst the protocols are equivalent for total carbon sampled on quartz fibre filters, "NIOSH EC was typically less than half of IMPROVE EC". Hansen (2005) also reported that data from the aethalometer calibrated against TOR (i.e. as used in the IMPROVE protocol) gave "numbers higher than BC" and that the TOT method (i.e. as used in the NIOSH protocol) gave results that differed markedly. It is not therefore unexpected that any calibrations based on these different protocols might also display the same differences. The comparison between the reflectometer and transmissometer measurements of the Emfab$^{TM}$ filters at Marylebone Road (2010 – 2012) were both calibrated against EC determined using the NIOSH-TOT protocol. Whilst the reduced major axis analysis reported in Table 5.7 above suggests that the reflectometer measurements continue to predict greater concentrations this is not borne out when comparing the range of concentrations set out in Table 5.8. The scatterplots (Figure 5.6) of these concentrations would seem to suggest that the transmissometer is more sensitive at lower levels of EBC but may be less so as EBC increases.

It is of interest to note that each method identified the same date as having maximum concentrations at each site.

*Table 5. 8* *Comparison of mean (arithmetic), minimum and maximum concentrations (μg $m^{-3}$) derived for EBC from both reflectometer and transmissometer measurements (quartz fibre and Emfab™ filter substrate)*

| **QUARTZ FIBRE FILTERS 2001 - 2005** | | | | |
|---|---|---|---|---|
| | **n** | **Minimum (date)** | **Mean (95% C.I.)** | **Maximum (date)** |
| | | **(μg $m^{-3}$)** | | |
| **Acton Town Hall (2001 – 2002)** | | | | |
| EBC (QR) | 273 | 0.5 (16.4.01) | 3.7 (3.5,4.0) | 12.1 (18.11.02) |
| EBC (QT) | 277 | 0.3 (28.4.02) | 2.5 (2.3 – 2.7) | 12.8 (18.11.02) |
| **Marylebone Road (2003 – 2005)** | | | | |
| EBC (QR) | 157 | 1.5 (14.8.05) | 8.7 (8.0,9.4) | 18.3 (28.10.03) |
| EBC (QT) | 157 | 1.3 (14.8.05) | 7.4 (6.8,8.0) | 16.5 (28.10.03) |
| **North Kensington (2003 – 2005)** | | | | |
| EBC (QR) | 115 | 0.08 (11.2.05) | 1.7 (1.4,1.9) | 11.3 (20.11.05) |
| EBC (QT) | 115 | 0.2 (4.4.05) | 1.4 (1.1,1.8) | 16.3 (20.11.05) |
| **EMFAB™ FILTERS (2010 – 2012)** | | | | |
| **Marylebone Road (2010 – 2012)** | | | | |
| EBC (ER) | 583 | 1.1 (26.9.10) | 6.8 (6.6,7.1) | 14.8 (30.9.10) |
| EBC (ET) | 583 | 1.2 (25.4.11) | 6.9 (6.7,7.1) | 14.2 (30.9.10) |

# Comparison with collocated NOx measurements

Road vehicles are a key source of ambient oxides of nitrogen (NOx) in the urban atmosphere (see, for example, Carslaw et al., 2011) and a correlation with ambient equivalent black carbon/elemental carbon concentrations at the same site would therefore be expected. Collocated contemporaneous measurements of NOx and EC (by either TOR or TOT) concentrations are available at Marylebone Road and Acton Town Hall. In the first instance these collocated concentrations have been compared to confirm that this relationship exists – see Figures 5.7 (a) and (b) and Table 5.9.

*Table 5.9 Reduced Major Axis relationships between collocated NOx and elemental carbon concentrations (NOx on the y axis)*

| Site | Sampling period | n | r | Gradient | Intercept |
|---|---|---|---|---|---|
| Acton Town Hall | 2001 – 2002 | 94 | 0.95 | 19.7±0.6 | -2.8±2.7 |
| Marylebone Road | 2010 - 2012 | 546 | 0.92 | 21.8±0.4 | 9.1±2.7 |

The concentrations of EBC determined above have been compared, using Reduced Major Axis correlation, with same day NOx concentrations at Marylebone Road, North Kensington and Acton Town Hall - see Table 5.10.

*Table 5.10 Reduced Major Axis relationships between collocated NOx and EBC (QT) or EBC (QR) concentrations (NOx on the y axis)*

| Site | Sampling period | n | EBC measurement | r | Gradient | Intercept |
|---|---|---|---|---|---|---|
| Acton Town Hall 2001 – 2002 | | 261 | EBC(QT) | 0.95 | 24.1±0.5 | -11.0±1.5 |
| | | | EBC(QR) | 0.95 | 21.1±0.4 | -7.0±1.8 |
| Marylebone Road 2003 - 2005 | | 156 | EBC(QT) | 0.94 | 21.2±0.6 | 3.1±4.6 |
| | | | EBC(QR) | 0.95 | 16.2±0.4 | 15.6±4.0 |
| North Kensington 2003 - 2005 | | 114 | EBC(QT) | 0.90 | 20.0±0.8 | 4.7±1.9 |
| | | | EBC(QR) | 0.87 | 24.0±1.1 | -6.5±2.5 |
| Marylebone Road 2010 - 2012 | | 581 | EBC(ET) | 0.84 | 29.5±0.7 | -46.2±5.0 |
| | | | EBC(ER) | 0.90 | 24.2±0.4 | -7.8±3.3 |

When comparing Tables 5.9 and 5.10, it is clear that the derived EBC concentrations in this study have similar relationships with NOx concentrations as the site measurements of elemental carbon and provide further confidence that they may be used to quantify EBC concentrations associated with traffic emissions. In addition the lack of intercept suggests that EBC, EC and NOx have the same source.

*Figure 5.7(a)* *Scatterplot of the relationship between EC (IMPROVE-TOR) concentrations and (same day) NOx concentrations at Acton Town Hall (2001 – 2002)*

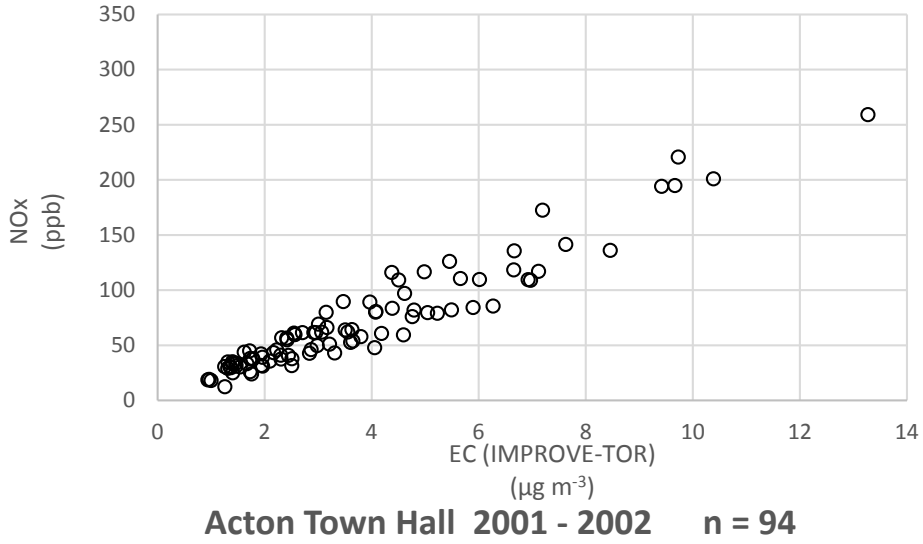
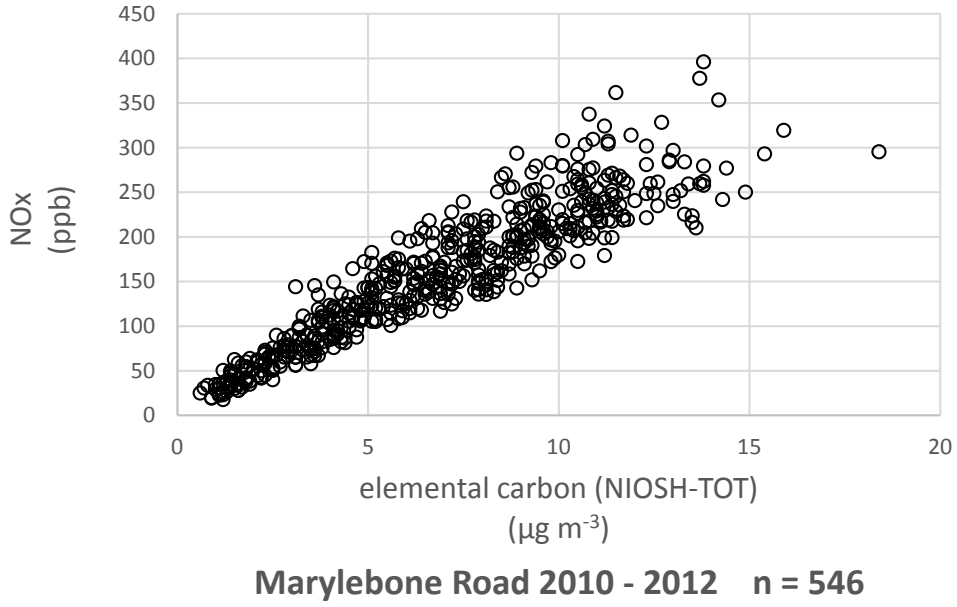



*Figure 5.7(b)* *Scatterplot of the relationship between EC (NIOSH-TOT) concentrations and (same day) NOx concentrations at Marylebone Road (2010 – 2012)*



## Choice of equation

In summary, in this chapter two light absorption methods, reflectometry and transmissometry, have been compared, both between each method and in relation to different filter substrates, against elemental carbon concentrations which have also been derived from two different protocols. This has resulted in the four different equations set out above. For this research project, it was necessary to decide which of these equations was the most appropriate for seeking to compare traffic emissions at different sites in London.

It was clear that either reflectometry or transmissometry would provide reasonable equivalent black carbon concentrations. It was considered that the transmissometer equations would provide more consistent comparable results for the following reasons:

- there was no need to compensate for the possible second reflectance of light back through the filter as only one beam of light is transmitted;
- the use of infrared rather than broadband light is a better indicator of light absorbing black carbon, and
- the elemental carbon measurement protocol (NIOSH-TOT) was consistent across filter substrates.

However, it was not considered appropriate to use the same equation for different filter substrates. It was decided that the following filter substrate specific equations provided the most appropriate conversion of the reflectometer and transmissometer measurements to an equivalent black carbon concentration:

**QUARTZ FILTERS:**

$$\mathbf{EBC\ (\mu g\ m^{-3}) = 0.8605((\ln(Io/I))^2) + 0.7382\ (\ln(Io/I))} \quad \textbf{(Equation 5.9)}$$

Where ln(Io/I) = Transmissometer ATN/100.

**EMFAB FILTERS:**

$$\mathbf{EBC\ (\mu g\ m^{-3}) = 0.3596\ ((\ln(Io/I))^2) + 4.8311(\ln(Io/I))} \quad \textbf{(Equation 5.13)}$$

Where ln(Io/I) = Transmissometer ATN/100.

These equations have been used to provide EBC concentrations (as defined above) at the study sites and the results are set out and discussed in the next chapter.

# Chapter 6

# Carbon sources in $PM_{10}$ as indicators of traffic emission variation in London 2001 - 2012

## Introduction

Many of the air quality initiatives implemented or considered over the last decade in London, e.g. the introduction of a Low Emission Zone in the Greater London area and proposals for an ultra-low emission zone in central London, have been aimed at reducing the impact of traffic emissions. It is therefore important to be able to consider whether there has been any reduction in these emissions to inform whether the thrust of these initiatives has been successful. However, also as previously discussed, it is more difficult to assess variation in these sources because, in the first instance, there is no regulatory requirement to do so. Nevertheless there are a number of research programmes which do measure atmospheric particulate carbon, a key indicator of traffic emissions in airborne particulate matter. Black carbon and elemental carbon are linked to traffic emissions and have been measured by different methods on a daily basis at two locations in London since 2008. They are both defined by their analysis method – see chapter 2 for details.

Many of the initiatives have been implemented since 2008 and therefore to be able to discern any variation it is necessary to have an indication of these sources prior to this time and this is more difficult to ascertain. In addition the impact of the initiatives may vary from place to place. Lenschow et al. (2001) pointed out that various locations will be more or less influenced by traffic emissions and therefore measurements of concentrations at two sites within a conurbation the size of London may not be wholly indicative of concentrations at different locations within the whole area. Traffic emission sources, due to their primary nature, are more likely to be local in origin in contrast to many of the other sources in PM, such as those discussed in chapter 4. The method set out in chapter 5 provides an opportunity to consider concentrations of these sources collected on time resolved archived PM filter samples at different sites.

There is also another historic dataset that could provide information about atmospheric particulate carbon sources. The Black Smoke Network in the UK and in particular in London also provides data across a long time period at different sites. Heal and Quincey (2012) provide an equation for converting black smoke concentrations to black carbon concentrations as follows:

$$\mathbf{BC\ (\mu g\ m^{-3}) = (0.27 \pm 0.03) * BSI_{(British)} - (4.0 \pm 0.2) * 10^{-4}\ BSI_{(British)}^{2}}$$

Some care, however, needs to be taken as to how far back the black smoke data might be considered representative of traffic emissions, bearing in mind that the method was introduced when the ubiquitous use of coal was the main source of atmospheric particulate carbon. As discussed in chapter 1 the morphology of black carbon particles arising from the incomplete combustion of coal and black carbon arising from traffic emissions, and in particular diesel, are different. However, by 1977 Ball and Hume noted that vehicles were the main source of "dark smoke" in the whole of the Greater London area and therefore it is considered reasonable to use the method derived by Heal and Quincey (2012) to indicate variation in traffic emission concentrations in London from 1990 onwards.

In this chapter, long term black smoke records at two sites in London: Greenwich High Road and Marylebone Road, are utilised and converted, as recommended by Petzold et al (2013) and discussed in chapter 5, to equivalent black carbon ('EBC') concentrations by applying the conversion determined by Heal and Quincey (2012). In this thesis, to distinguish these concentrations from those derived from the equations determined in chapter 5, these concentrations will be referred to as EBC (BS). These are then compared to equivalent BC (EBC (QT) and EBC (ET)) concentrations at Acton Town Hall (2001 – 2002), Marylebone Road (2003 – 2005, 2010 – 2012), North Kensington (2003 – 2005) and Oxford Street (2011- 2012) derived from the method set out in chapter 5 and using the datasets already discussed in chapters 3 and 4. To recap the following equations have been used to derive EBC (QT) and EBC (ET) concentrations at each site:

**QUARTZ FILTERS:**

$$\mathbf{EBC(QT)\ (\mu g\ m^{-3}) = 0.8605\ ((\ln(Io/I))^2) + 0.7382\ (\ln(Io/I))} \quad \textbf{(Equation 5.9)}$$

where ln(Io/I) = Transmissometer ATN/100.

**EMFAB FILTERS:**

$$\mathbf{EBC(ET)\ (\mu g\ m^{-3}) = 0.3596\ ((\ln(Io/I))^2) + 4.8311(\ln(Io/I))} \quad \textbf{(Equation 5.13)}$$

where ln (Io/I) = Transmissometer ATN/100.

As PM10 and PM2.5 are the only species currently regulated, it is important to be able to consider the contribution of atmospheric particulate carbon sources to variation in airborne PM as well. The PM10 data has therefore been binned in 10 μg $m^{-3}$ concentrations (in the same way as carried out in chapters 3 and 4) and site comparisons made.

# Results and Discussion

## Equivalent black carbon concentrations derived from historic black smoke measurements ('EBC (BS)')

Figures 6.1 and 6.2 are the time series plots for equivalent black carbon concentrations (EBC (BS)) at Greenwich High Road between 1990 and 2008 and Marylebone Road between 1999 and 2009. One of the strengths of using this conversion is that the method of analysis by reflectometry to determine the original black smoke concentration has not changed over time nor has the filter substrate. Therefore the changes in concentrations may confidently be regarded as indicators of changes in traffic exhaust emissions or other sources of 'black carbon'.

EBC (BS) at Greenwich High Road seems to show an apparent step change in concentrations at the end of the 1990's. It is also difficult to detect whether there might have been changes as a result of the introduction of the Low Emission Zone in 2008 as monitoring finished at about the same time. Nevertheless it may be seen from the trend analysis (TheilSen) in Figure 6.3 over the whole period there is a significant downward trend of approximately 0.13 $\mu g\ m^{-3}$ per year amounting to an overall reduction of approximately 50%. The data have been disaggregated between the two periods 1990 to 1999 and 2000 to 2008 (i.e. where it would seem the change occurred) and each period subjected to the same trend analysis to ascertain whether this trend continued after 2000 as there almost appears to be two populations in the analysis in Figure 6.1. As may be seen from Figure 6.4 a significant downward trend continued after 2000 but was lower than the period 1990 - 1999. Prior to 2000 the downward trend was approximately 0.2 $\mu g\ m^{-3}$ per year amounting to a reduction during the period 1990 to 1999 of approximately 50%. The annual reduction more than halved during the period 2000 to 2008 and was approximately 0.08 $\mu g\ m^{-3}$ per year but still resulted in concentrations reducing annually by almost a further 50%.

It is not known whether any specific traffic management or other schemes, including the opening of the Docklands Light Railway extension to Greenwich, might be responsible for the apparent step change in concentrations from 2000 onwards. Further investigation using CUSUM (Barratt et al., 2007) might prove fruitful to identify the change date but has not been carried out as part of the research in this project

*Figure 6.1* *Time series of EBC(BS) concentrations, Greenwich High Road, 1990 – 2008 n = 5866*

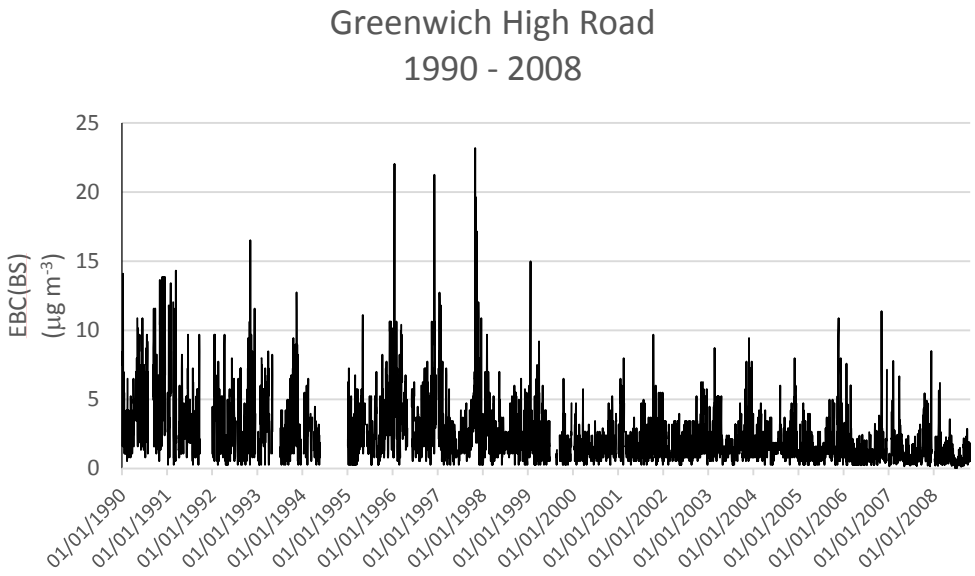



*Figure 6.2* *Time series of EBC(BS) concentrations, Marylebone Road, 1999 – 2009 n = 2502*

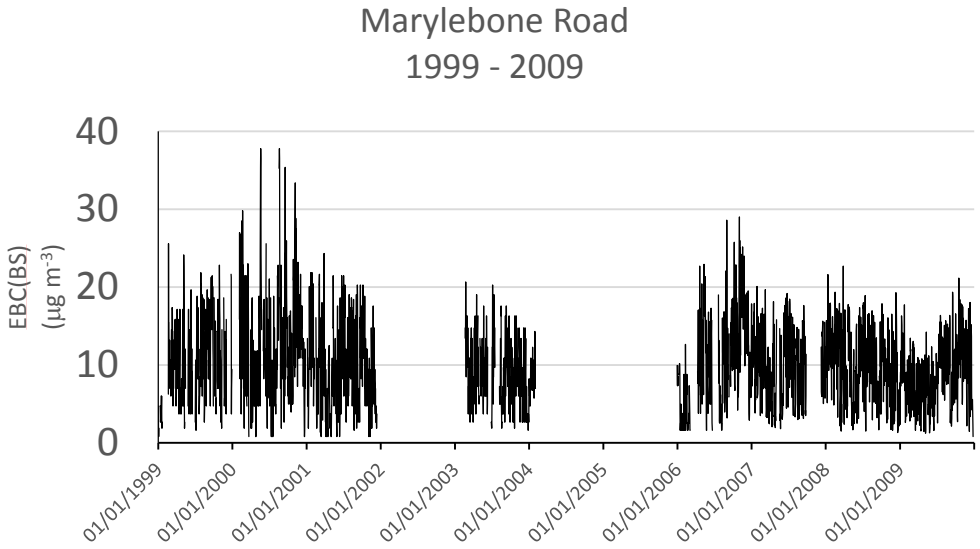


*Figure 6.3 TheilSen analysis, EBC(BS) concentrations, Greenwich High Road 1990 – 2008, n = 5866*

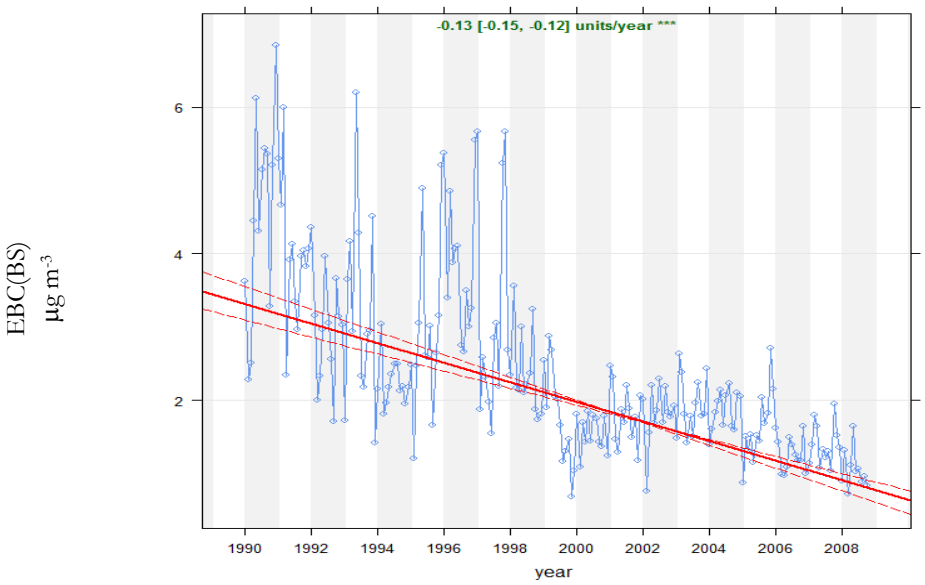
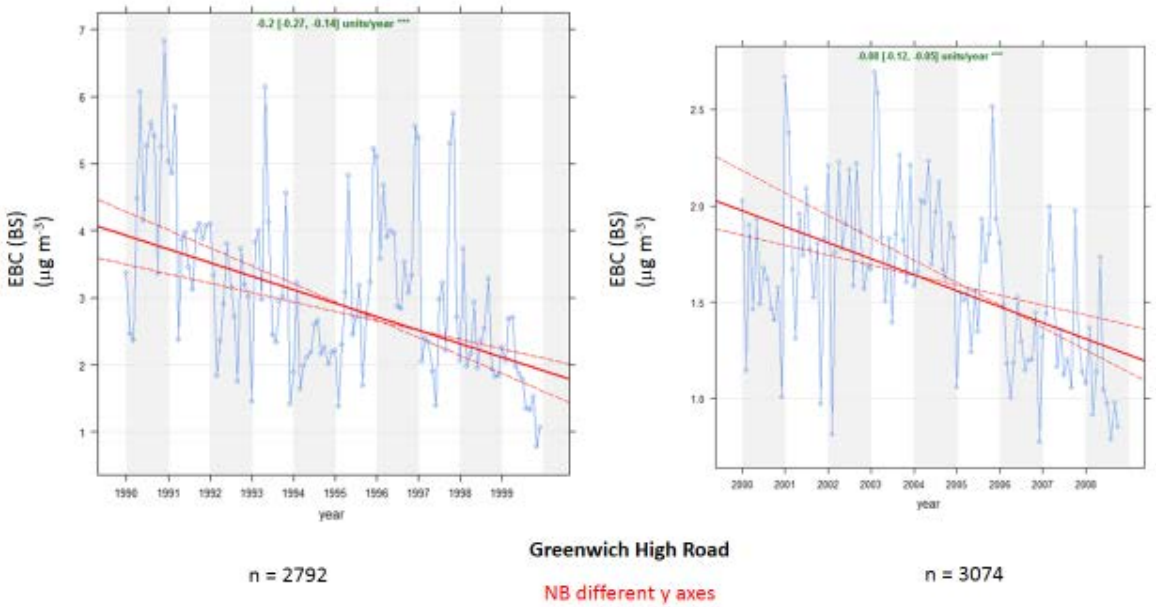



*Figure 6.4 TheilSen analysis, EBC(BS) concentrations, Greenwich High Road (a) 1990 – 1999 and (b) 2000 -2008*

*(a)* *(b)*



In contrast to the trends reported in respect of Greenwich High Road there would appear to be no obvious long-term trend in the concentrations at Marylebone Road (Figure 6.2) and indeed this is confirmed in the trend analysis in Figures 6.5 and 6.6. For this analysis the data have been separated between 1999 – 2001 and 2006 – 2009 as there is little intervening data to perform an adequate trend analysis (see Figure 6.2). These time periods could however be indicative of change as they occur after the implementation of the new regulatory regime and during the introduction of the LEZ. No significant trend is detected in either time period.

Details of the trend analysis at Greenwich High Road and Marylebone Road together with the mean concentrations for each analysis period are set out in Table 6.1 below. The difference in the mean concentrations at Greenwich High Road between 1990/1999 and 2000/2008 support the trend analysis (3.1 to 1.6 μg $m^{-3}$). However it should be noted that at Marylebone Road there was a decrease in mean concentrations between the two trend analysis periods (i.e. between 2001 and 2006) which amounts to approximately 11%.

*Table 6.1 EBC (BS) trends and arithmetic mean concentrations (μg $m^{-3}$) , Greenwich High Road, 1990 – 2008 and Marylebone Road, 1999 – 2009.*

| Site | Sampling period | No of sample days | Overall trend (μg $m^{-3}$) per year (95% C.I.) | p | Mean concentration (whole sampling period) (μg $m^{-3}$) (95% C.I.) |
|---|---|---|---|---|---|
| Greenwich High Road | 1990 - 1999 | 2792 | -0.2 (-0.27, -0.14) | <0.001 | 3.1 (3.0,3.2) |
| | 2000 - 2008 | 3074 | -0.08 (-0.12, -0.05) | <0.001 | 1.6 (1.55,1.63) |
| Marylebone Road | 1999– 2001 | 908 | -0.56 (-1.71, +0.63) | >0.1 | 11.0 (10.6, 11.4) |
| | 2006 – 2009 | 1291 | -0.3 (-1.24, +0.48) | >0.1 | 9.7 (9.4,10.0) |

*Figure 6. 5 TheilSen analysis, EBC(BS) concentrations, Marylebone Road 1999 - 2001*

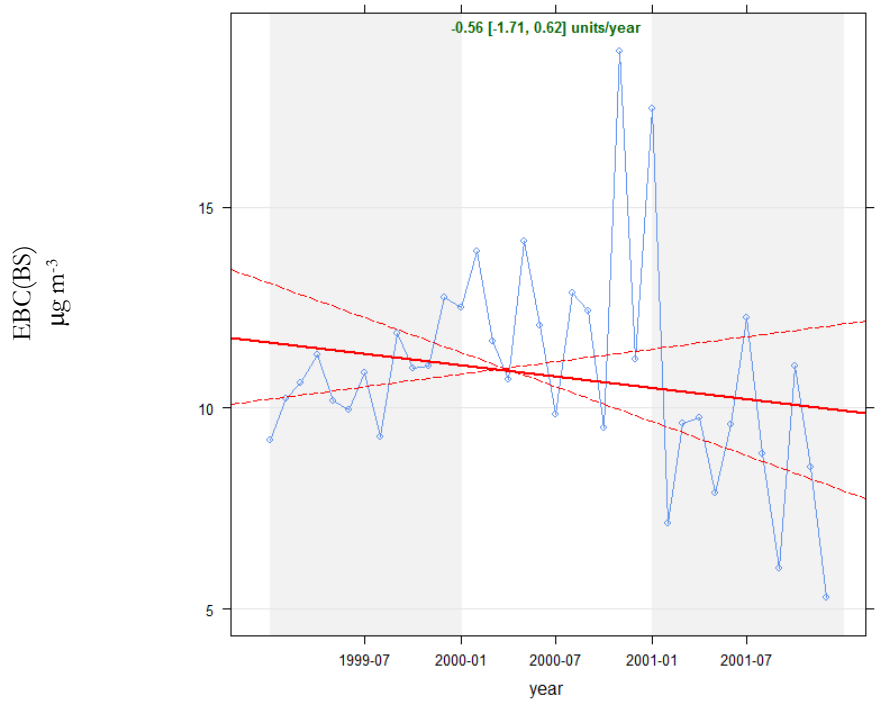



*Figure 6.6 TheilSen analysis, EBC(BS) concentrations, Marylebone Road 2006 - 2009*

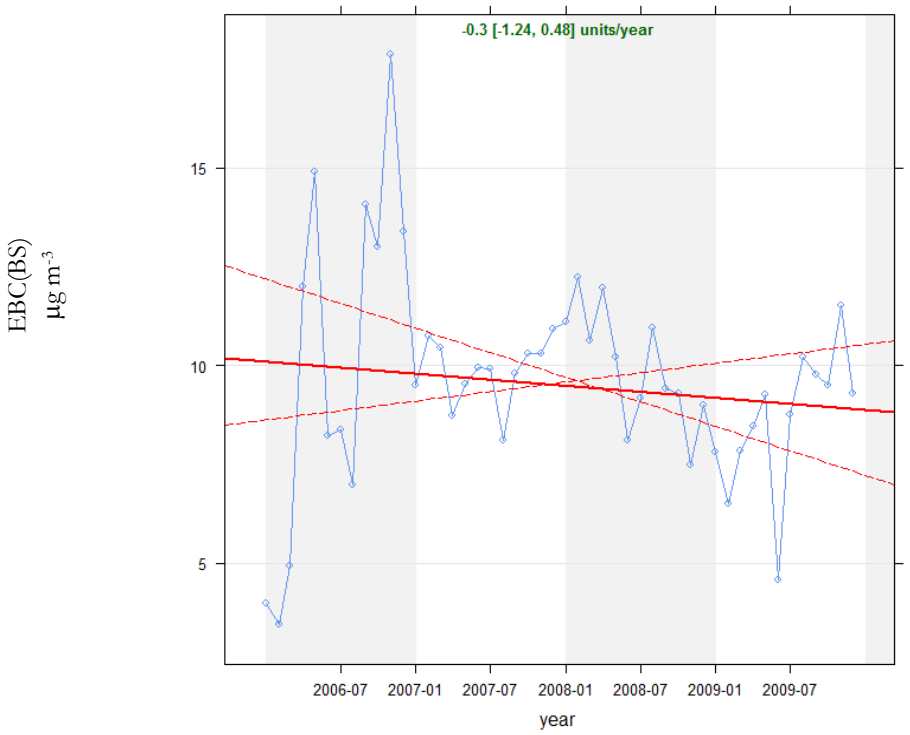
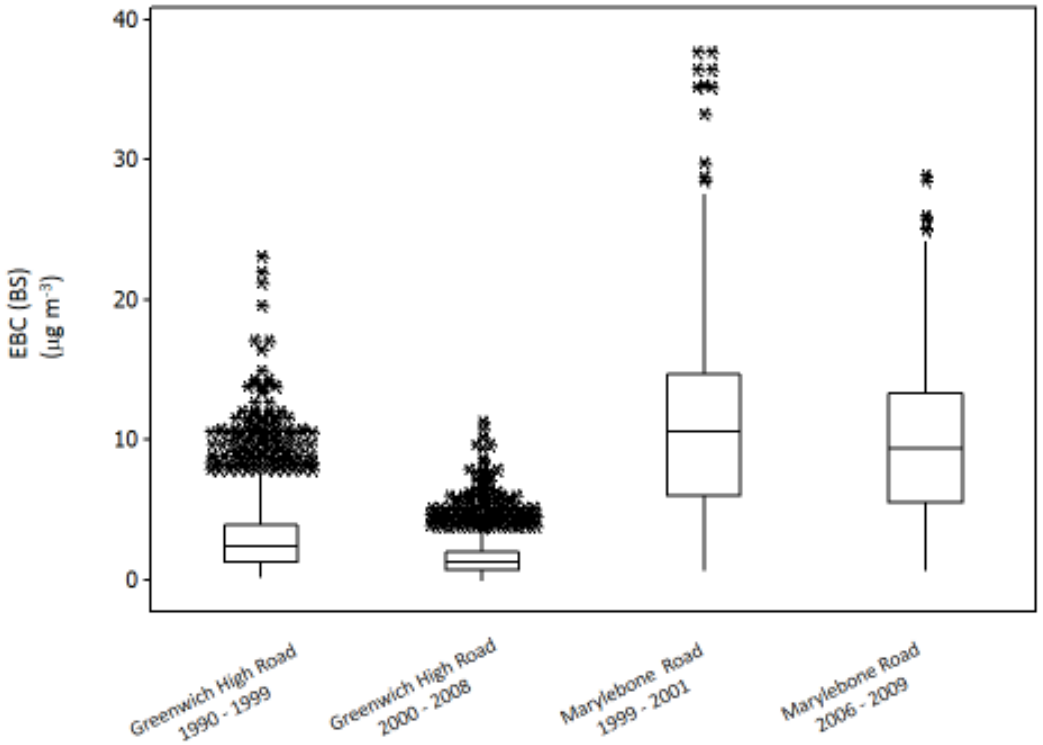


Figure 6.7 is box plots of the datasets used in the trend analysis discussed above. Greenwich High Road had overall lower EBC (BS) concentrations than Marylebone Road and the decrease between 1999 and 2008 is demonstrable. There were an apparent larger number of outliers in the Greenwich High Road dataset but there were also more sample days (see Table 6.1 above). Nevertheless there were occasions when concentrations were in the same magnitude as concentrations at Marylebone Road.

*Figure 6.7* *Box plots illustrating distribution of EBC (BS) concentrations at Greenwich High Road 1990 – 2008 and Marylebone Road 1999– 2009.*



## *Day of the week and monthly variation in EBC (BS) at Greenwich High Road and Marylebone Road*

Figures 6.8 (a) and (b) demonstrate the day of the week mean (arithmetic) differences in EBC (BS) concentrations at each location. There is an approximate 25% reduction in concentrations at Greenwich High Road on Sundays compared with other days of the week and an approximate 30% commensurate reduction at Marylebone Road. Reductions which occur regularly on a Sunday must only be as a result of human activity as no natural activity would repeat in this particular cycle. Despite the differences in overall concentrations the percentage reduction is very similar at both locations probably as a result of lower commercial vehicular use and reduced public transport. It is also interesting to note that there would appear to be a greater reduction in mean concentrations on Saturdays at Marylebone Road. This may be due to a reduction of commercial vehicles being used on a Saturday in central London that also probably occurs in Greenwich but balanced by an increase in local traffic.

Seasonal differences in monthly mean (arithmetic) concentrations are shown in Figures 6.9 (a) and (b). There is a clear reduction in concentrations at Greenwich High Road during the summer months and the higher concentrations in the winter months are probably due to increased vehicular use (potentially private use) together with a contribution from local heating systems. There was also likely to be less dispersion during the longer winter nights and temperature inversions may well have prevented dispersion. No similar pattern emerges from a comparison of the monthly mean concentrations at Marylebone Road where concentrations seemed to be at their lowest during April each year. As concentrations are also low in December these might be linked to reductions of commercial traffic during the Easter and Christmas breaks.

*Figure 6.8 day of the week variation in mean concentrations of EBC(BS) at (a) Greenwich High Road 2001 – 2008 and (b) Marylebone Road 1999- 2008*

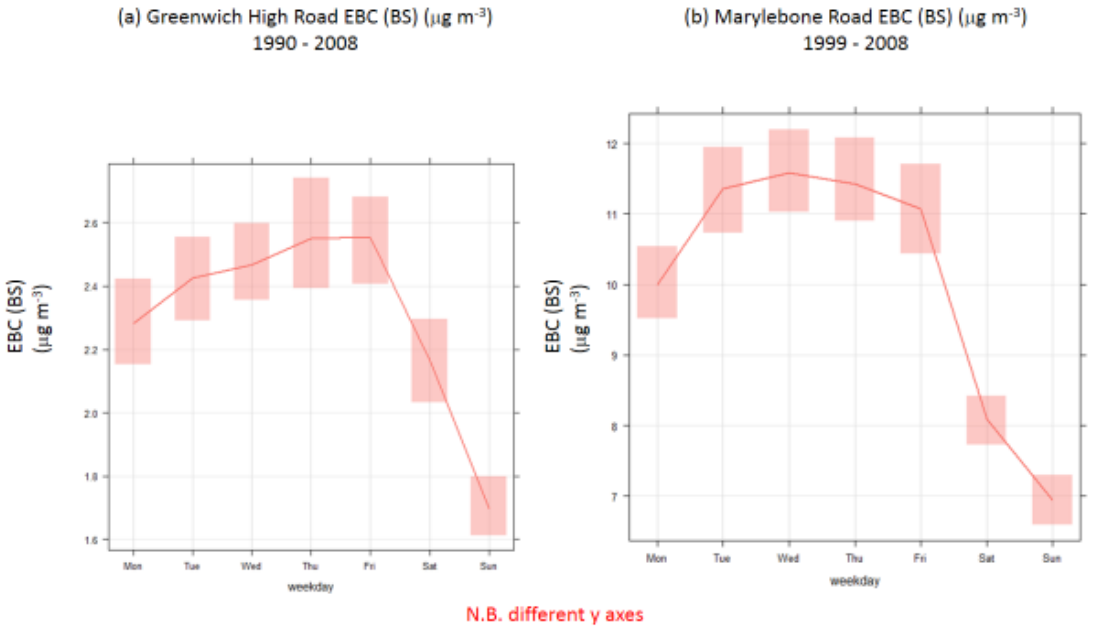
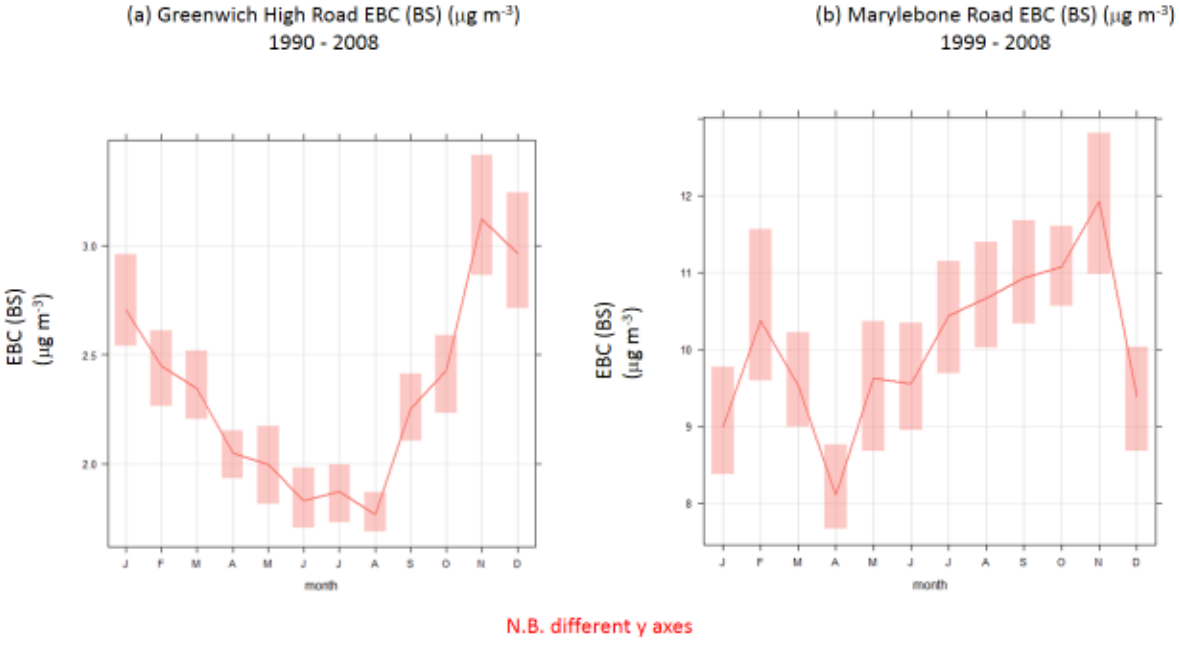



*Figure 6.9 monthly variation in mean concentrations of EBC(BS) at (a) Greenwich High Road 2001 – 2008 and (b) Marylebone Road 1999- 2008*



## Equivalent black carbon (EBC) concentrations derived from time resolved Partisol filters

It is of interest to be able to compare the results of the EBC (BS) concentrations reported above with the EBC (QT) and (ET) concentrations but it must be noted that the equations obtained in each method are derived from different methods of atmospheric carbon analysis (namely 'real-time' aethalometer black carbon for EBC (BS) and NIOSH-TOT elemental carbon analysis of time resolved quartz filters). As may be seen from the scatterplots in Figure 6.10, and as reported by Butterfield et al. (2010) there is a clear relationship between the daily concentrations of black carbon and elemental carbon at both North Kensington and Marylebone Road (2010 – 2012) as would be expected. The regression equations derived by reduced major axis regression analysis at each site are

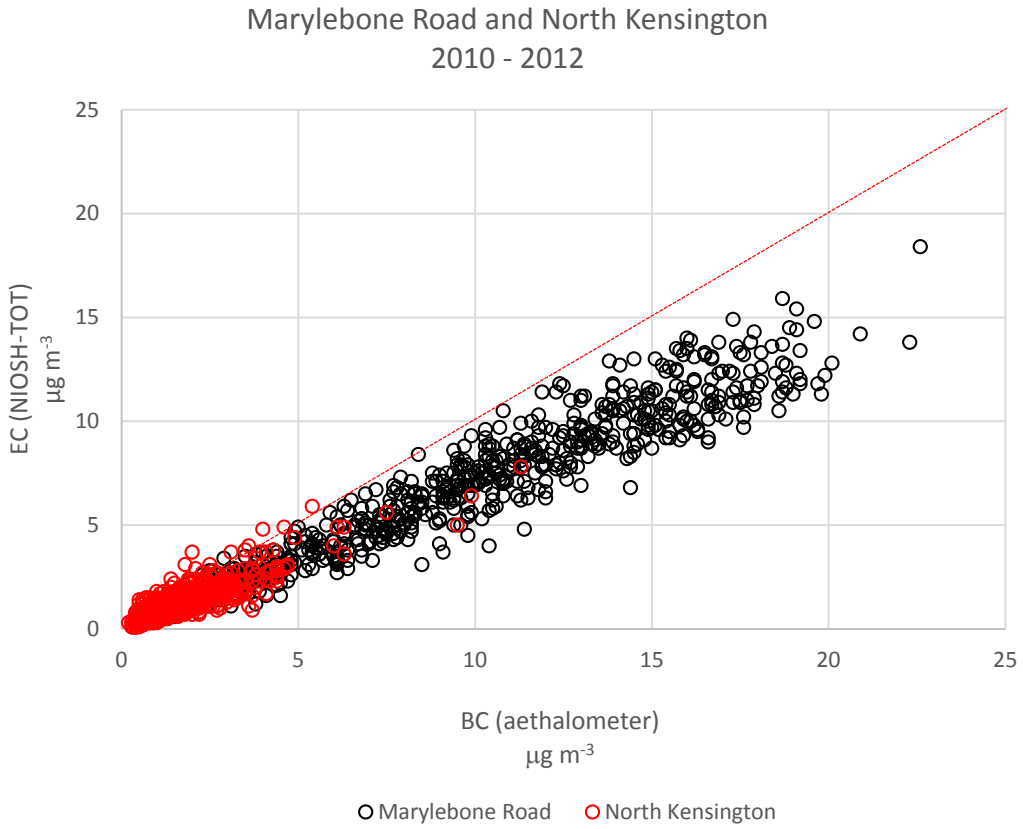
North Kensington. EC ($\mu g\ m^{-3}$)= 0.83 BC – 0.10 r 0.88 . n = 956

Marylebone Road. EC ($\mu g\ m^{-3}$)= 0.72 BC – 0.20 r 0.96 . n = 664

( where EC = elemental carbon measured by the NIOSH-TOT method
and BC = black carbon measured by aethalometer)

It needs to be borne in mind therefore that when making comparisons based on these measurements, at these sites, the reported BC concentrations are approximately 1.3 greater than the EC concentrations for the same day. As discussed in chapter 5 the default $\sigma_{ATN}$ for aethalometers used in the Black Carbon Network is 16.6 $m^2\ g^{-1}$ but Hansen (2005) in the Aethalometer operator manual recognises that $\sigma_{ATN}$ would be different if ATN were calibrated against EC measurements. This analysis would seem to support this suggestion and would result in $\sigma_{ATN}$ of approximately 11 – 12 $m^2\ g^{-1}$ which is similar to the EC $\sigma_{ATN}$ in Hansen (2005).

*Figure 6.10* *Scatterplots comparing EC (NIOSH-TOT) concentrations and BC (aethalometer) concentrations measured at Marylebone Road and North Kensington 2010 - 2012*



## EBC (QT) concentrations at Acton Town Hall 2001 – 2002; North Kensington and Marylebone Road, 2003 - 2005

Equivalent black carbon (EBC (QT)) concentrations (μg $m^{-3}$) derived from quartz fibre PM filter samples (Partisol 2025) at Acton Town Hall, North Kensington and Marylebone Road between 2001 and 2005 have been calculated using the following equation (and based on transmissometer measurements):

$$\textbf{EBC (QT) (μg m}^{-3}\textbf{)} = 0.8605\,((\ln(Io/I))^2) + 0.7382\,(\ln(Io/I)) \quad \textbf{Equation 5.9}$$

Where ln(Io/I) = Transmissometer ATN/100.

Time series of the EBC (QT) concentrations at each site are shown in Figures 6.11, 6.12, and 6.13. Boxplot comparisons of the concentrations are shown in Figure 6.14. As set out in chapter 5 there were elemental carbon measurements also available at Acton Town Hall between 2001 and 2002 derived by the IMPROVE-TOR method but no equivalent transmissometer measurements of these filters. It has been decided not to incorporate these concentrations into the EBC (QT) concentrations reported in Figure 6.11 and discussed in this section because there are differences between the IMPROVE-TOR method and the NIOSH-TOT method (that has been used for the EBC calibration in this project), as outlined by Chow et al. (2001) and discussed in chapter 5, such that the concentrations from the two methods may not be inter-convertible. It should also be noted that the concentrations at Acton Town Hall are based on measurements from the fine ($PM_{2.5}$) filter sample in a Partisol 2025 dichotomous sampler.

*Figure 6.11 Time Series, EBC (QT) concentrations (µg m$^{-3}$), Acton Town Hall, 2001 - 2002*

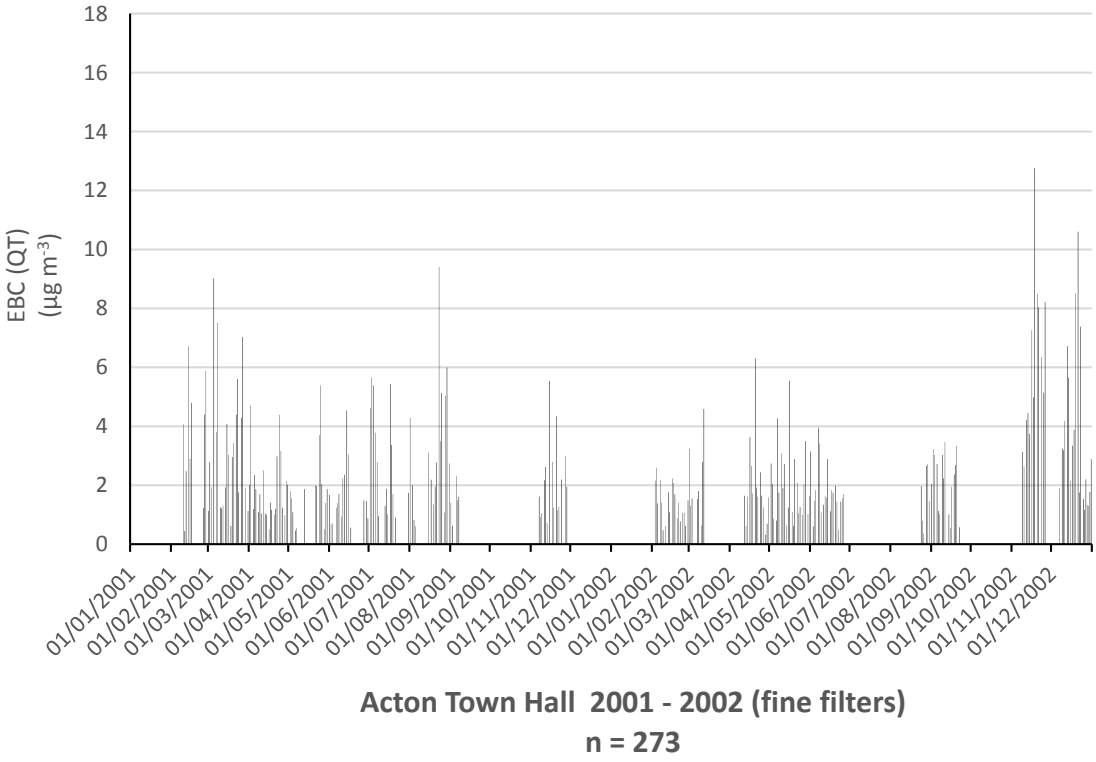



*Figure 6.12 Time Series, EBC (QT) concentrations (µg m$^{-3}$), North Kensington, 2003 - 2005*

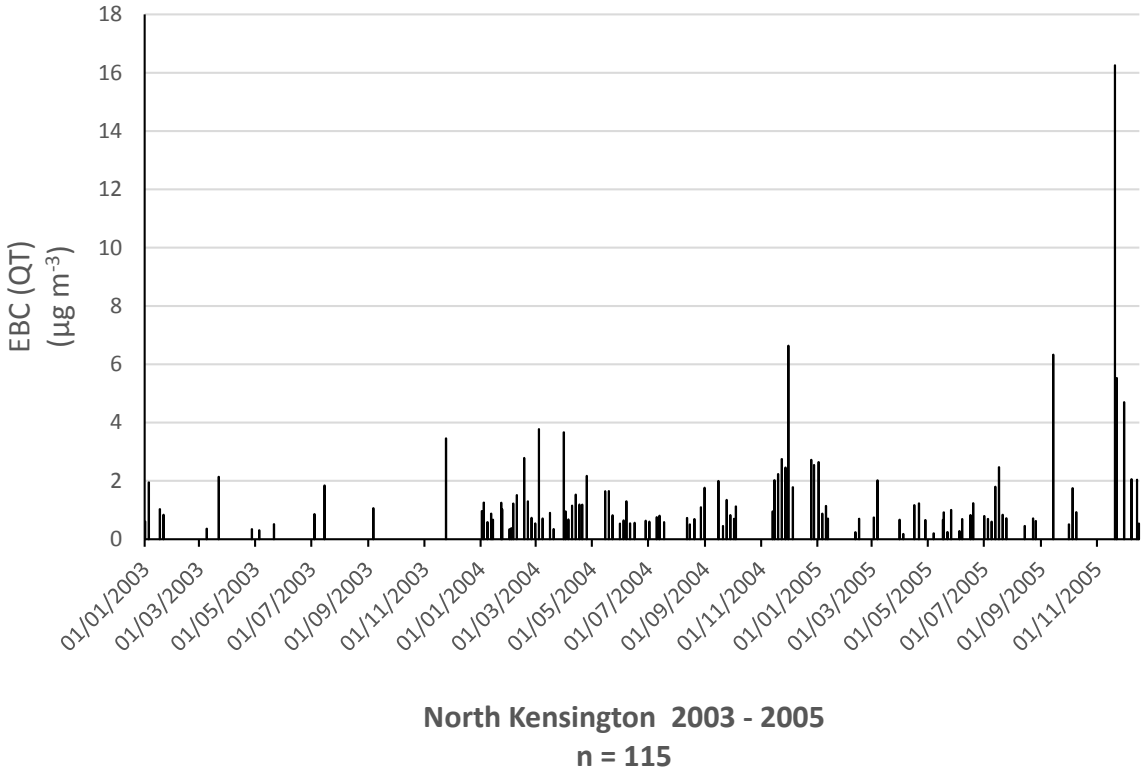


*Figure 6.13 Time Series, EBC (QT) concentrations (μg m$^{-3}$) Marylebone Road 2003 - 2005*

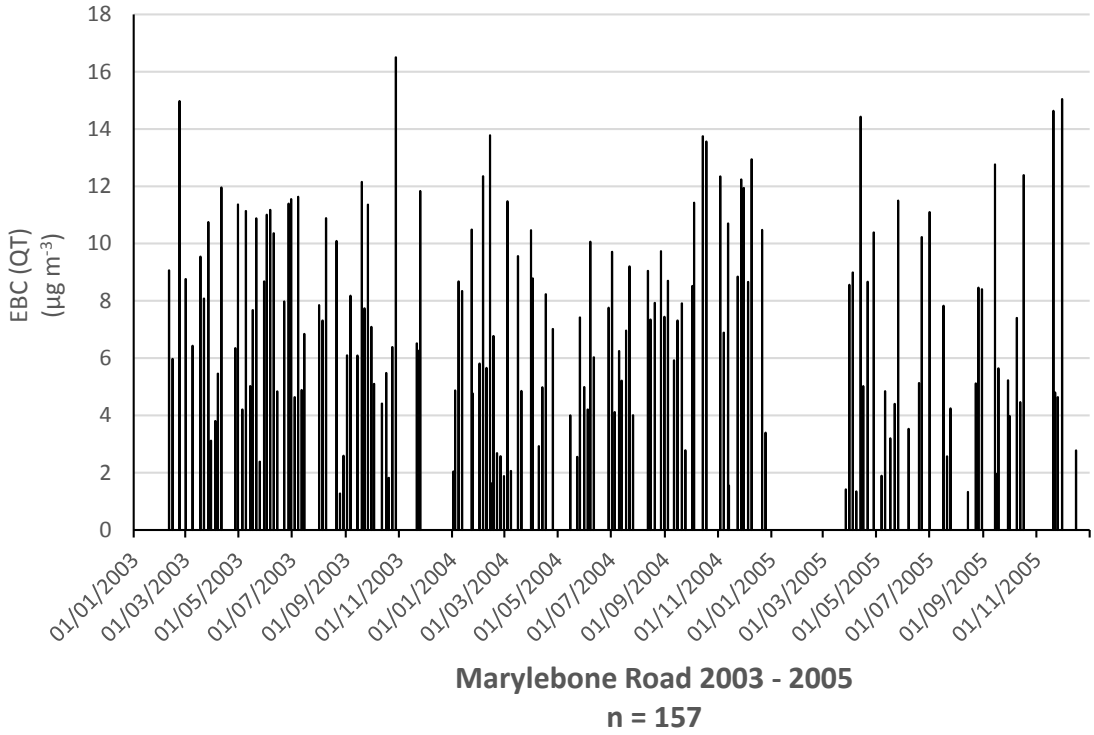
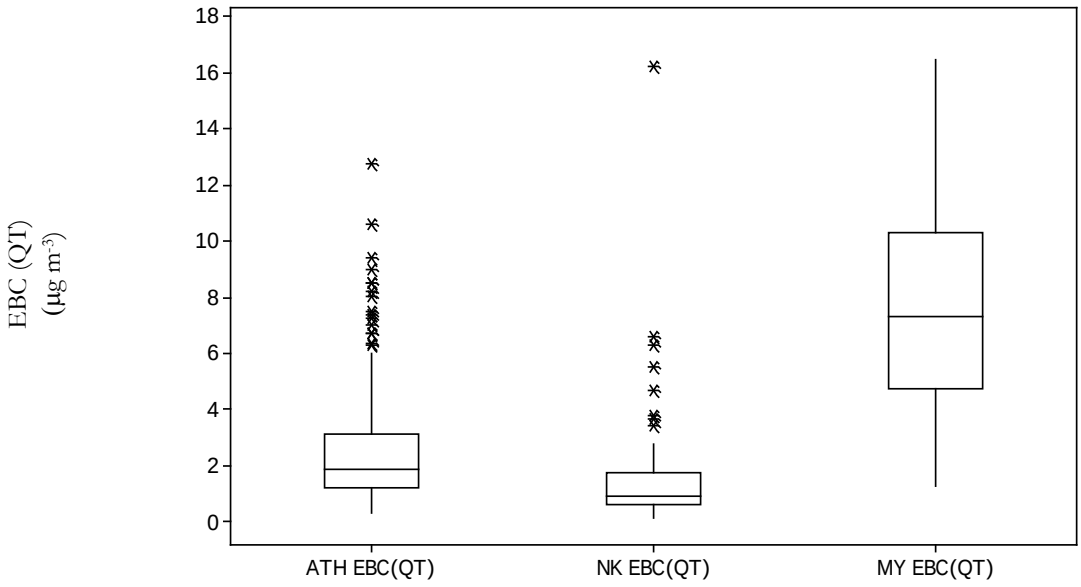



*Figure 6.14 Box plots illustrating distribution of EBC (QT) concentrations (μg m$^{-3}$) Acton Town Hall 2001 – 2002, North Kensington 2003 – 2005 and Marylebone Road, 2003 - 2005*




Where ATH EBC (QT) = Acton Town Hall, 2001 – 2002
NK EBC (QT) = North Kensington 2003 – 2005
MY EBC(QT) = Marylebone Road 2003 - 2005

Table 6.2 sets out details of the EBC (QT) concentrations determined at each site. As expected, the mean concentrations at Marylebone Road seem to be lower than the EBC (BS) concentrations as a result of the different carbon measurement method used for the calibration, as discussed above. There are differences in mean concentrations at each site and there would appear to be a clear 'Lenschow' hierarchy with the lowest concentrations at the urban background site.

*Table 6.2 EBC (QT) concentrations (μg m$^{-3}$): Acton Town Hall, North Kensington and Marylebone Road 2001 - 2005*

| **Site** | **Sampling period** | **No of sample days** | **Mean (95%C.I.'s)** | **Maximum (date)** |
|---|---|---|---|---|
| | | | (μg m$^{-3}$) | |
| Acton Town Hall | January 2001 – December 2002 | 273 | 2.5 (2..3 – 2.7) | 12.8 (18.11.02) |
| North Kensington | 2003 – 2005 | 115 | 1.4 (1.1, 1.8) | 16.3 (20.11.05) |
| Marylebone Road | 2003 - 2005 | 157 | 7.4 (6.8,8.0) | 16.5 (28.10.03) |

At North Kensington there is one concentration which stands out as being significantly higher than the other measurements. As already discussed in chapter 5, this concentration occurred on Sunday 20 November 2005 when a daily mean $PM_{10}$ concentration of 92.5 μg m$^{-3}$ was also recorded. The co-located TEOM recorded a 'spike' in $PM_{10}$ concentrations in the early hours of the morning and, whilst there is no record of what might have caused it, it is considered unlikely to have been related to traffic exhaust emissions.

Trend analysis (TheilSen) at each site is shown in Figures 6.15, 6.16, 6.17 (a) and (b) and summarised in Table 6.3. Unlike the EBC (BS) concentrations at Greenwich High Road described above there would appear to be no significant trend in EBC (QT) concentrations at Acton Town Hall during 2001 to 2002 but it is a relatively short timescale with gaps in the series being considered. At Marylebone Road there is a significant downward trend ($p<0.1$). There is however one particularly low concentration recorded on 16 December 2005 (and indeed is the only datapoint in that month, thus representing the monthly average). With this datapoint removed the trend becomes -0.42(-1.01, 0.38) and is no longer significant, similar to the EBC (BS) concentrations reported above. There was no significant trend in concentrations at the background site at North Kensington between 2003 and 2005 but it is possible that the high concentrations recorded on 20 November 2005 mentioned above are skewing data. To test this, this date and 3 other dates in November 2005 when EBC(QT) concentrations above 4 $\mu g\ m^{-3}$ were recorded were removed and the calculations repeated and whilst, as may be seen, the trend becomes significant ($p<0.05$) there is one further low datapoint which might also be skewing the data but no further analysis with this datapoint omitted was made. In summary no statistically significant trends in any direction of EBC emissions are discernible at any of the three sites between 2001 and 2005 but all trends tend downwards. This could point to underlying decreases in BC emissions which might be discernible with more data or a longer analysis period.

*Table 6.3 EBC (QT) TheilSen trend analysis and statistical significance, Acton Town Hall 2001 – 2002, North Kensington 2003 – 2005, Marylebone Road 2003 – 2005*

| Site | Sampling period | No of sample days | Trend ($\mu g\ m^{-3}$) per year (95% C.I.) | p |
|---|---|---|---|---|
| Acton Town Hall | 2001 – 2002 | 273 | -0.03 (-1.14, +0.77) | >0.1 |
| Marylebone Road | 2003 - 2005 | 157 | -0.54 (-1.24, +0.01) | <0.1 |
| North Kensington | 2003 - 2005 | 115 | -0.06 (-0.21, +0.15) | >0.1 |
| | | 111 | -0.14 (-0.3, -0.02) | <0.05 |

*Figure 6.15 TheilSen analysis, EBC (QT)concentrations, Acton Town Hall 2001 – 2002 n = 273*

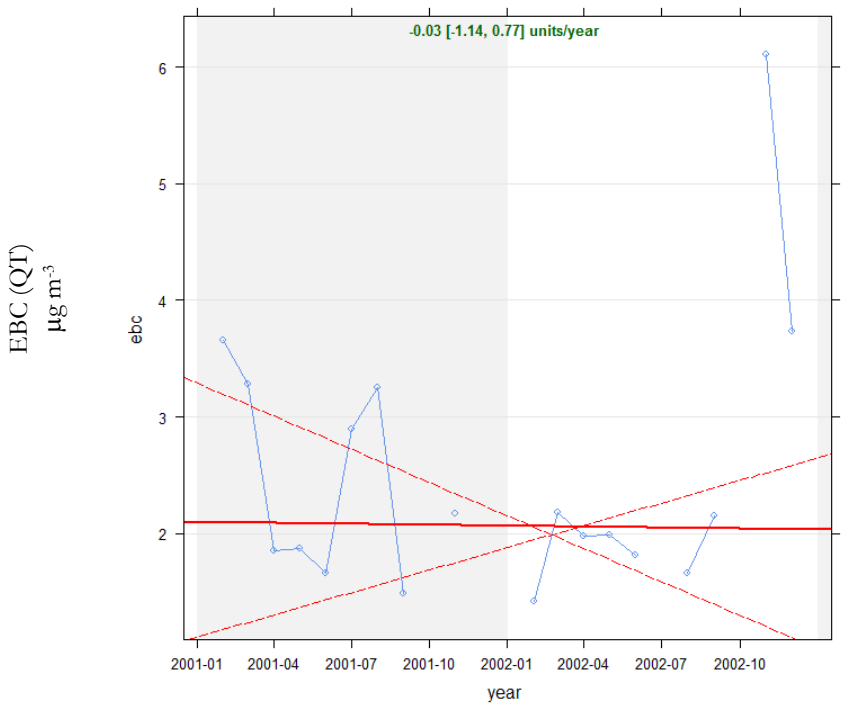



*Figure 6.16 TheilSen analysis, EBC (QT) concentrations, Marylebone Road 2003 – 2005 n = 157*

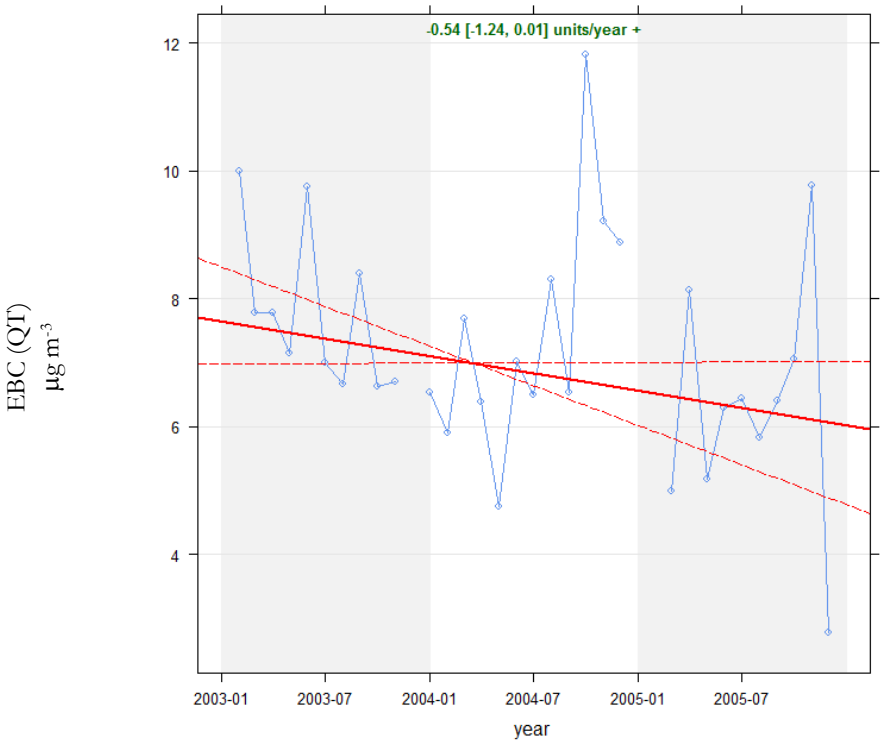
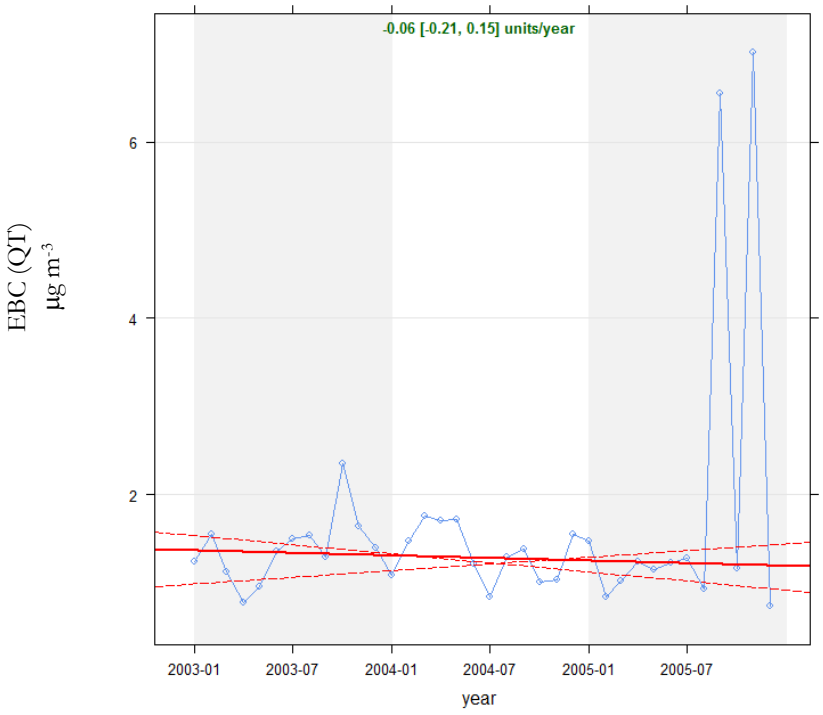
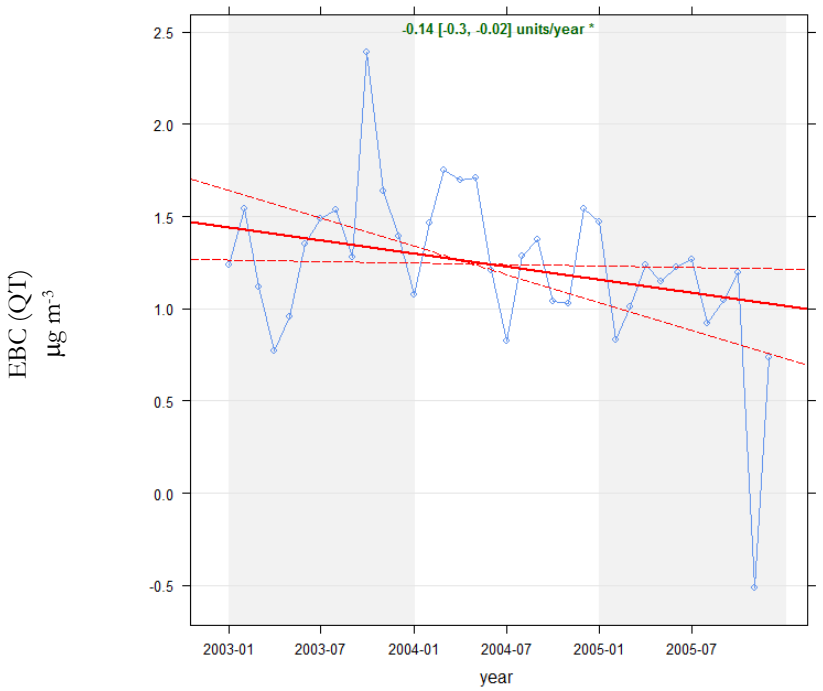


*Figure 6.17 TheilSen analysis, EBC (QT) concentrations, North Kensington 2003 – 2005*

*(a) n = 115*




*(b) n = 111 (4 datapoints in November 2005 removed – see text for explanation)*



## *Day of week and monthly variation in EBC (QT) at Acton Town Hall, 2001 – 2002; and Marylebone Road and North Kensington 2003 - 2005*

Day of week variation at each of the three sites are shown in Figures 6.18 and 19 (a) and (b). At Acton Town Hall, in line with the EBC (BS) measurements reported above, there was a reduction in EBC (QT) concentrations of approximately 50% on Sundays compared with the weekdays during the study period. The trend is not obvious at North Kensington or Marylebone Road, and indeed if the reported concentration for Sunday 20 November 2005 were included in the analysis for North Kensington there would have been a rise in mean concentrations. Additionally, concentrations were very low at North Kensington as it is an urban background site and therefore small fluctuations would seem to make bigger differences. At all three sites there was a large range in concentrations on each day of the week and it is therefore difficult to distinguish any weekday pattern in emissions.

Seasonal variation, as illustrated in Figures 6.20 and 6.21, was different at all three sites. Acton Town Hall had a similar seasonal pattern to Greenwich High Road although there was a rise in the summer months of July and August that was not discernible at Greenwich High Road. This is probably explained by the paucity of data available for these months at Acton Town Hall. There were 19 days with concentration values in July 2001 and none for July 2002 and similarly there were only 9 sampling days in August 2002 (and 23 in August 2001). Sampling did not occur during the whole of December 2001 as well. It is therefore difficult to be confident about seasonal trends at Acton Town Hall. At North Kensington the data may be skewed by the high concentrations recorded in November but there seemed to be little seasonal variation. Similarly at Marylebone Road no seasonal variation was demonstrable, indicative of its nature as a heavily trafficked central London highway.

*Figure 6.18 day of week variation, EBC (QT), Acton Town Hall, 2001 - 2002*

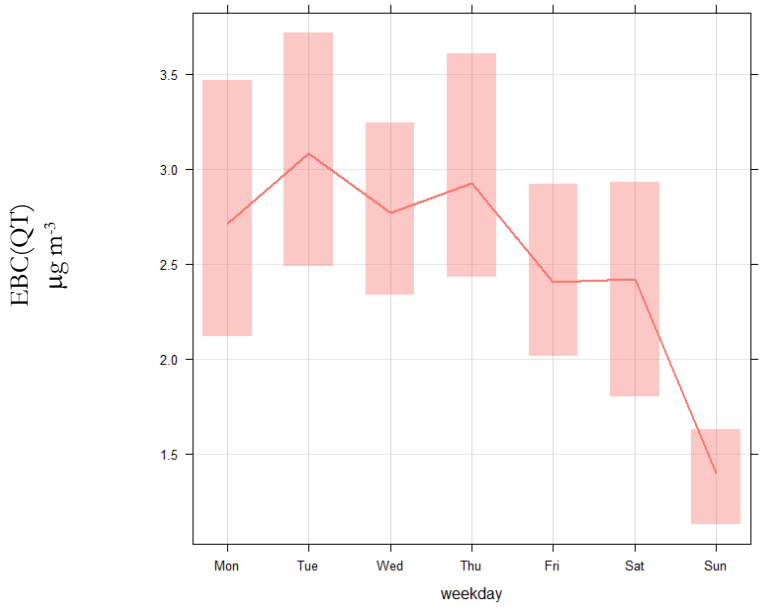



*Figure 6.19 day of week variation, EBC (QT) (a) North Kensington 2003 – 2005 and (b) Marylebone Road 2003 – 2005*

*(a)* *(b)*

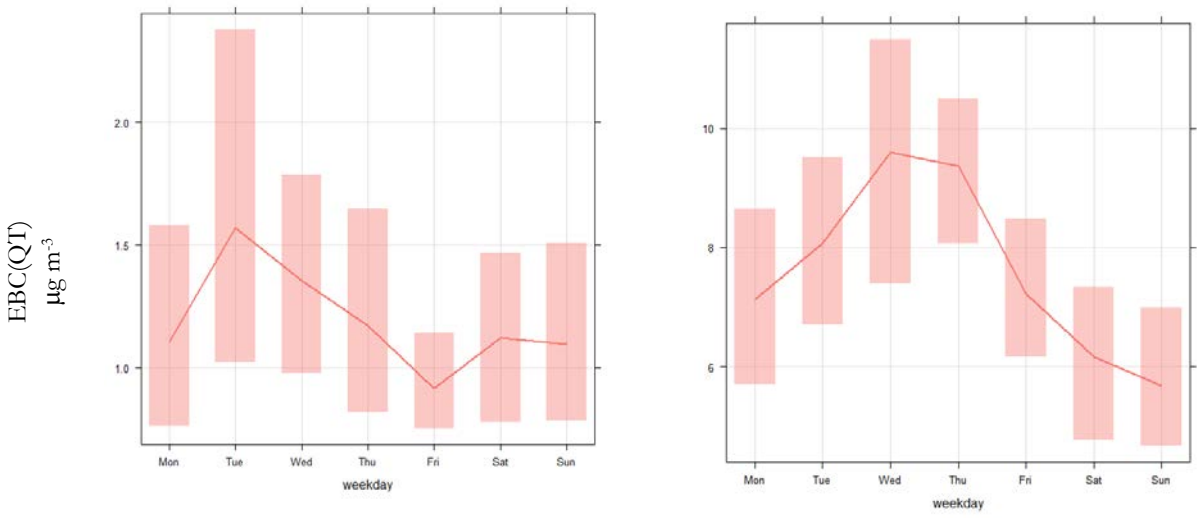


*Figure 6.20 monthly variation, EBC (QT) concentrations, Acton Town Hall 2001 - 2002*

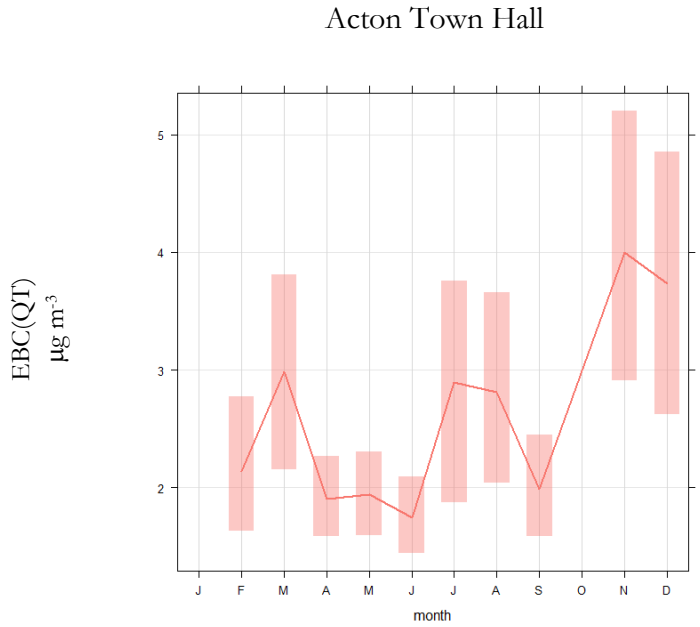
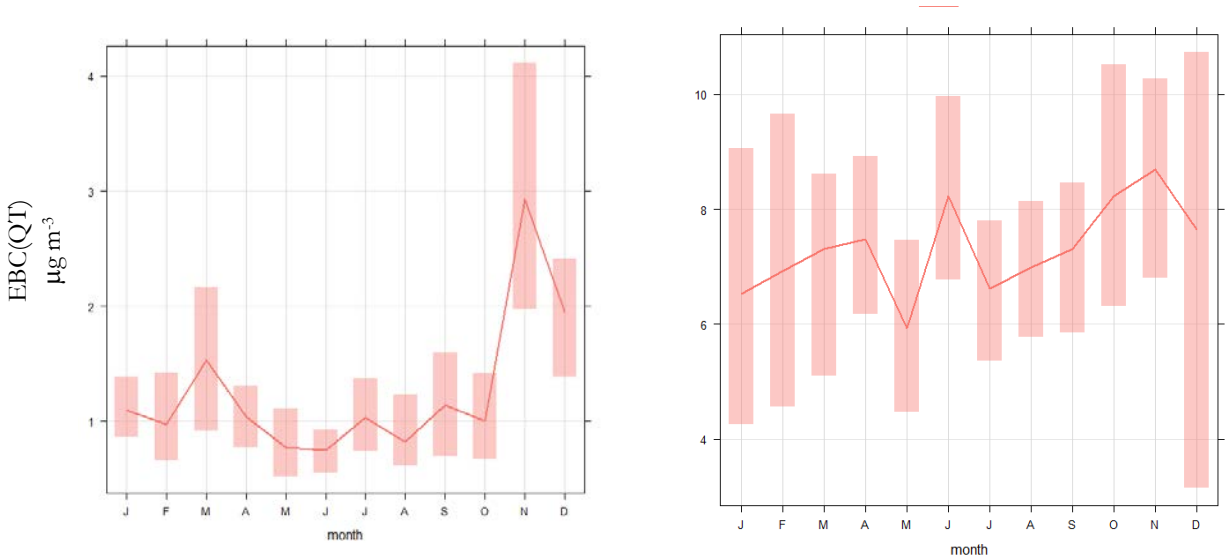



*Figure 6.21 monthly variation, EBC (QT) (a) North Kensington 2003 – 2005 and (b) Marylebone Road 2003 – 2005*

*(a)* *(b)*



## EBC (ET) concentrations at Marylebone Road 2010 – 2012 and Oxford Street 2011 - 2012

Equivalent black carbon (EBC (ET)) concentrations (μg $m^{-3}$) derived from Emfab™ PM filter samples (Partisol 2025) at Marylebone Road between 2010 and 2012 and Oxford Street between 2011 and 2012 were calculated using the following equation (and based on transmissometer measurements):

$$\textbf{EBC (μg m}^{-3}\textbf{)} = 0.3596\,((\ln(Io/I))^2) + 4.8311(\ln(Io/I)) \qquad \textbf{Equation 5.13}$$

Where lnIo/I = Transmissometer ATN/100.

Time series of the EBC (ET) concentrations at each site are shown in Figures 6.22 and 6.23. Boxplot comparisons of the concentrations are shown in Figure 6.24. Table 6.4 presents the mean concentrations determined at each location. For clarity, there are more sample days at Marylebone Road available for this analysis than were used in chapter 5 (n = 583) because EC concentrations were not available for every filter sample day.

*Table 6.4 EBC (ET) concentrations (μg $m^{-3}$): Marylebone Road 2010 – 2012 and Oxford Street 2011 – 2012*

| Site | Sampling period | No of sample days | Mean (95%C.I.) | Maximum (date) |
|---|---|---|---|---|
| | | | (μg $m^{-3}$) | |
| Marylebone Road | January 2010 to June 2012 | 614 | 6.9 (6.6,7.1) | 14.0 (30.9.10) |
| Oxford Street | January 2011to July 2012 | 540 | 6.4 (6.3,6.6) | 13.1 (20.11.11) |

When comparing the EBC concentrations at these two sites, the two datasets appear to be very similar. Mean and maximum concentrations are comparable and the range of concentrations was very similar. This is perhaps not surprising considering both are busy central London roads but there is one very important distinction. Marylebone Road is a heavily trafficked 6 lane highway with an arterial function as a route for traffic, commercial and private, into and out of London. Oxford Street has a very different function. It is a busy world-renowned shopping street, with a large number of pedestrians, where the only permitted vehicular traffic are diesel-powered buses and taxis (McCreanor et al., 2007).

*Figure 6.22, Time Series, EBC (ET) concentrations, Marylebone Road January 2010 to June 2012*

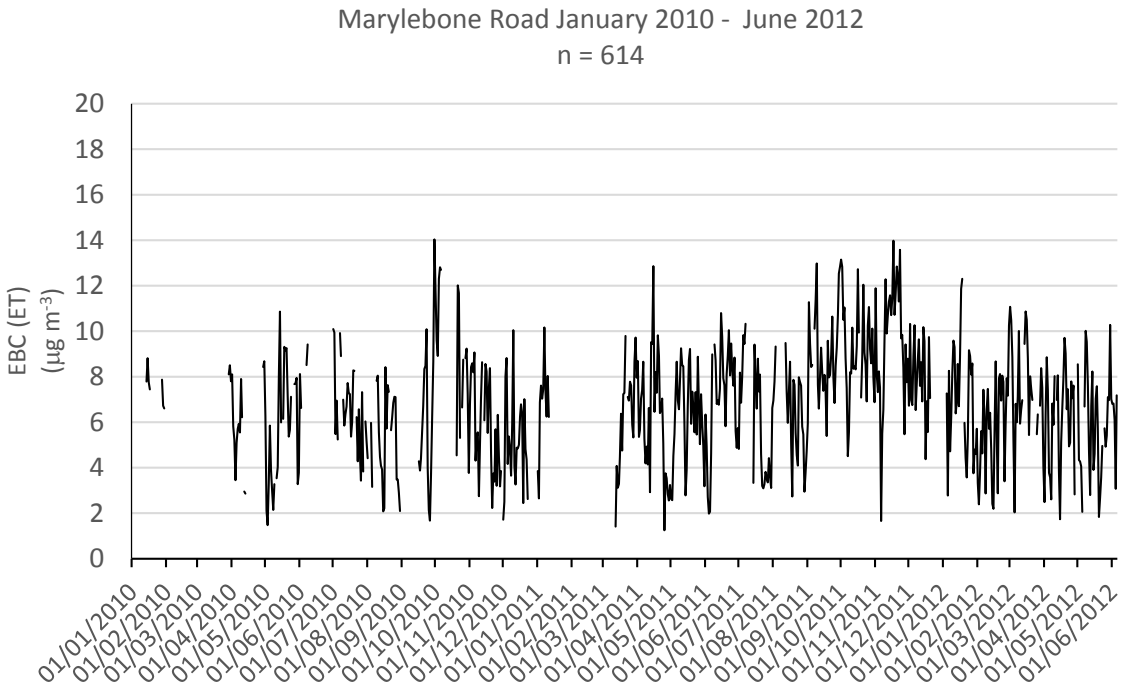



*Figure 6.23 Time Series, EBC (EBT) concentrations, Oxford Street, January 2011 – July 2012*

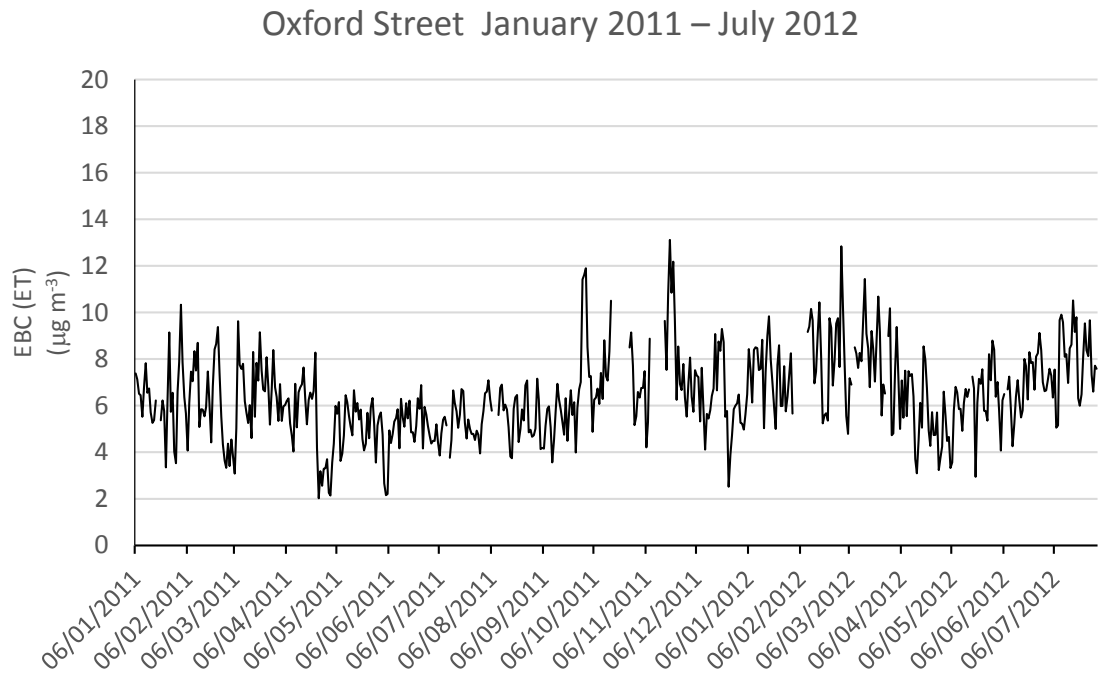
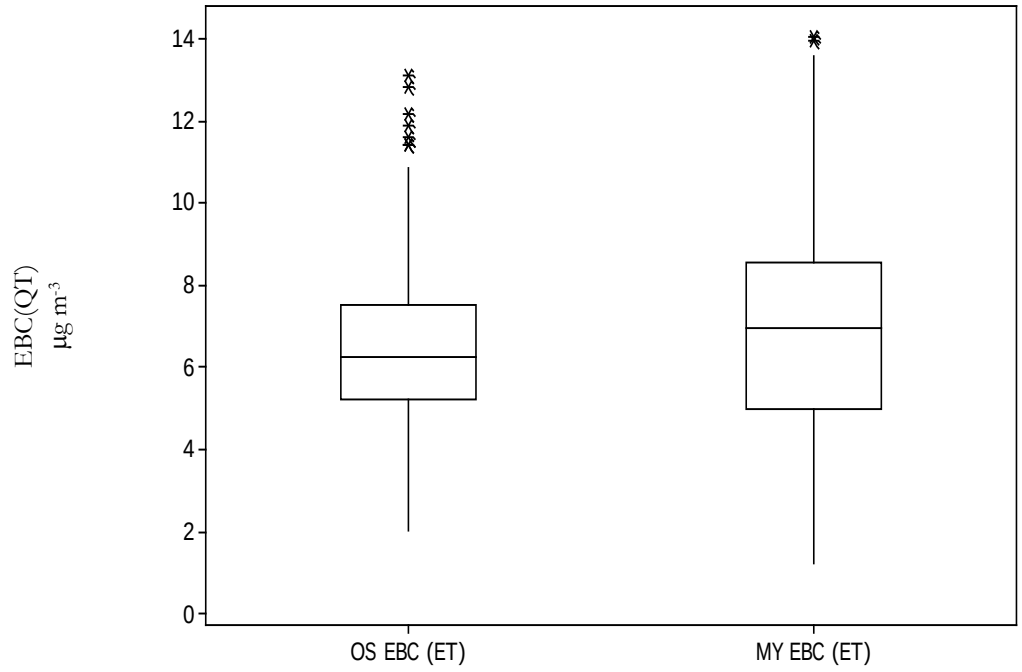


*Figure 6.24* *Boxplots comparing EBC(ET) concentrations, Oxford Street, 2011 – 2012 and Marylebone Road, 2010 – 2012*




OS EBC (ET) = Oxford Street 2001 - 2012

MY EBC (ET) = Marylebone Road 2010 - 2012

Trend analysis of concentrations at each site is demonstrated in Figures. 6.25 and 6.26 and reported in Table 6.5. The most striking and surprising observation is the distinctive difference between the two trends. At Marylebone Road between 2010 and 2012 there was no clear trend in EBC concentrations in any direction but this is in marked contrast to the trends in EBC concentrations at Oxford Street which were demonstrating a significant ($P<0.01$) upward trend. Bearing in mind that many of the initiatives introduced in London, discussed in chapter 1, targeted traffic exhaust emissions it might perhaps have been hoped that a trend in the opposite direction would be demonstrable.

*Table 6.5 EBC (ET) trend analysis and statistical significance, Marylebone Road 2010 – 2012, Oxford Street 2011 – 2012*

| **Site** | **Sampling period** | **No of sample days** | **Trend (μg m$^{-3}$) per year (95% C.I.)** | **p** |
|---|---|---|---|---|
| Marylebone Road | January 2010 to June 2012 | 614 | -0.25 (-0.58, +0.16) | >0.1 |
| Oxford Street | January 2011to July 2012 | 540 | +1.18 (0.32, 2.38) | <0.01 |

*Figure 6.25 TheilSen analysis, EBC (ET) concentrations, Marylebone Road 2010 - 2012*

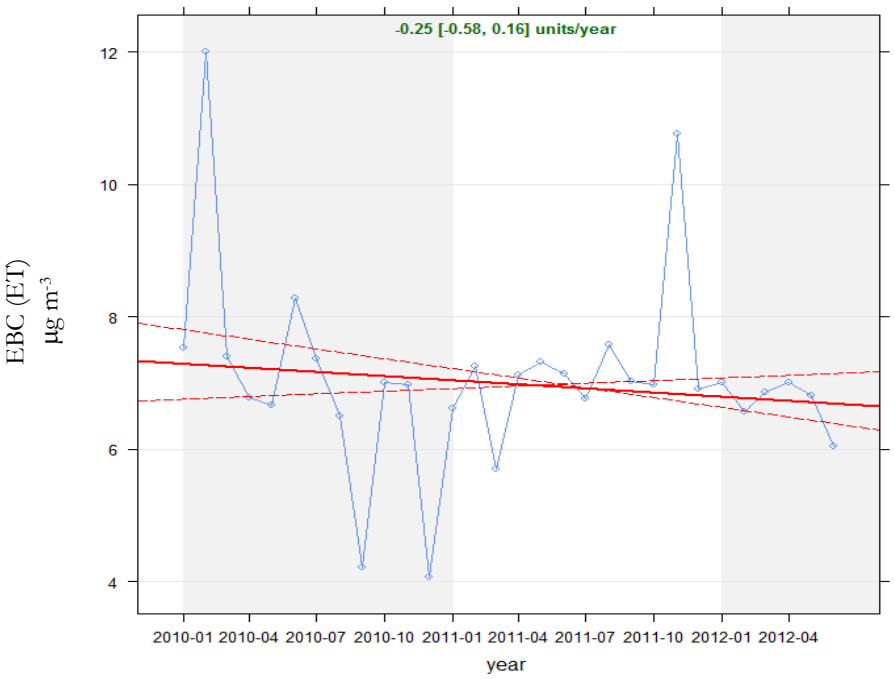
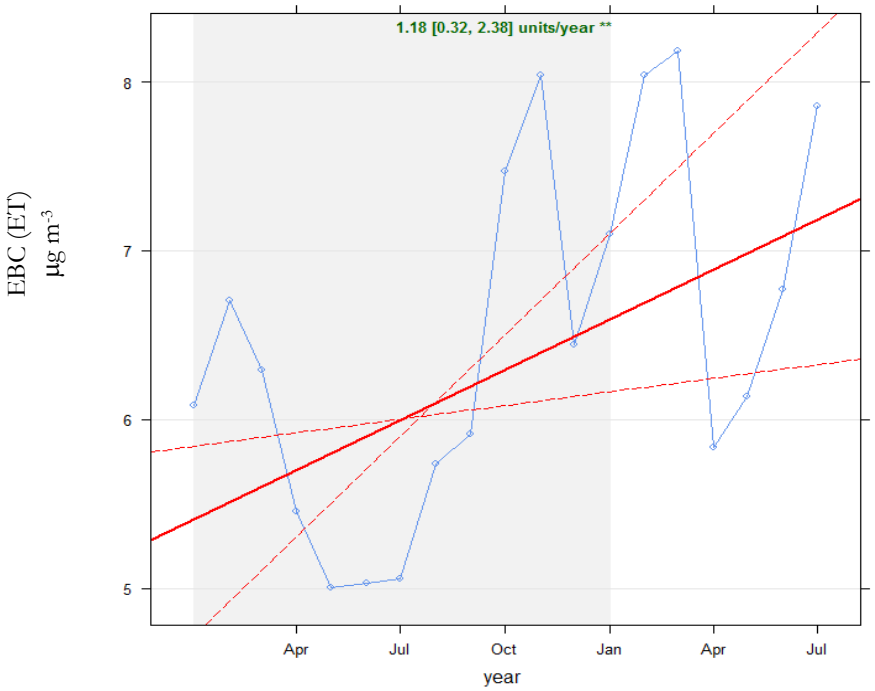



*Figure 6.26 TheilSen analysis, EBC (ET) concentrations, Oxford Street 2011 - 2012*



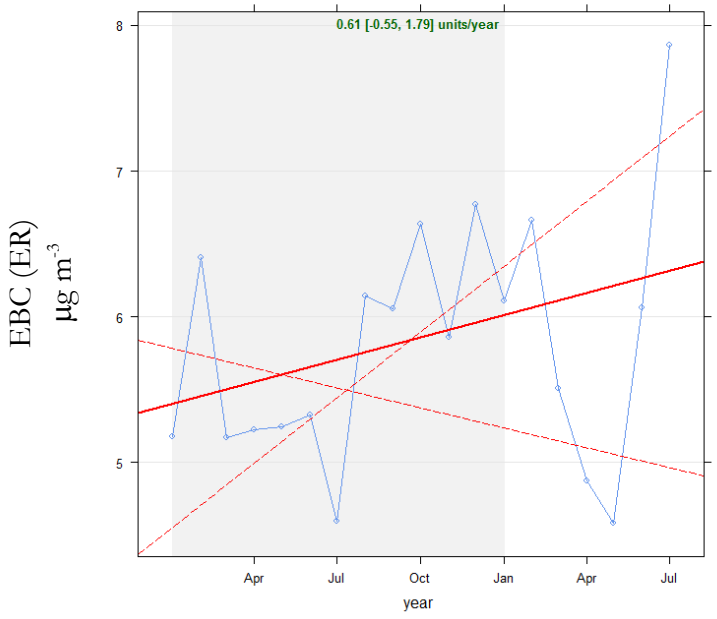
In order to check that the original filter measurements made using the transmissometer are accurate, the reflectometer measurements of the same filters were converted to EBC(ER) concentrations using the equation obtained from empirical observation, and reported in chapter 5, as follows:

$$\mathbf{EBC(ER)\ (\mu g\ m^{-3}) = 0.7707 * \ln(Ro/R)^2 + 2.1082 * \ln(Ro/R)} \quad \textbf{Equation 5.11}$$

The trend analysis of the EBC(ER) concentrations derived from this equation is demonstrated in Figure 6. 27. An upward trend (+0.61 µg $m^{-3}$ per year) remains.

PM10 concentrations at Oxford Street were not increasing (see chapter 3, Figure 3.18). However, buses were on diversion at the start of 2011 due to the Crossrail works taking place and therefore EBC concentrations may have been reduced. If this is the case then the increase once buses were reusing Oxford Street strongly supports Westminster City Council's proposal in its Air Quality Action Plan (2013) to prioritise tackling traffic emissions in key areas such as Oxford Street.

*Figure 6.27, TheilSen analysis, EBC(ER) concentrations, Oxford Street 2011 – 2012 (for comparison with Figure 6.26: EBC (ET) concentrations at the same site)*



## *Day of the week and monthly variation in EBC (ET) Marylebone Road 2010 – 2012 and Oxford Street 2011 - 2012*

Day of the week and monthly concentrations are shown in Figures 6.28 and 6.29 in respect of Marylebone Road 2010 – 2012 and Oxford Street 2011 – 2012.

Day of the week variation in concentrations of EBC (ET) at both sites was similar with mean concentrations falling within a very narrow range (Marylebone Road: 5.6 – 7.7 μg $m^{-3}$; Oxford Street: 5.1 – 6.6 μg $m^{-3}$). At both sites concentrations reduce by approximately 20% on Sundays but there was a more noticeable reduction on Saturdays at Marylebone Road when compared to Oxford Street.

It is possible to compare these daily concentrations at Marylebone Road with those derived from filters sampled between 2003 and 2005 in Figure 6.16 and the EBC (BS) concentrations illustrated in Figure 6.4. The daily variation between EBC (BS) and EBC (ET) was very similar (although EBC (ET) concentrations are lower for the reasons discussed above). Daily variation in the concentrations determined between 2003 and 2005 (Figure 6. 19) seem to show less of a reduction on Sundays compared to weekdays but there are fewer sample days in that dataset.

Seasonal variation between Marylebone Road and Oxford Street was similar although Oxford Street has lower concentrations in summer. This seasonality was not as apparent however as it was in the concentrations determined at Greenwich High Road (Figure 6.9) or Acton Town Hall (Figure 6.18).

At both Marylebone Road and Oxford Street the highest concentrations were determined in the autumn months.

*Figure 6 28. Day of the week variation, EBC (ET) (μg m$^{-3}$) Marylebone Road 2010 – 2012, Oxford Street, 2011 - 2012*

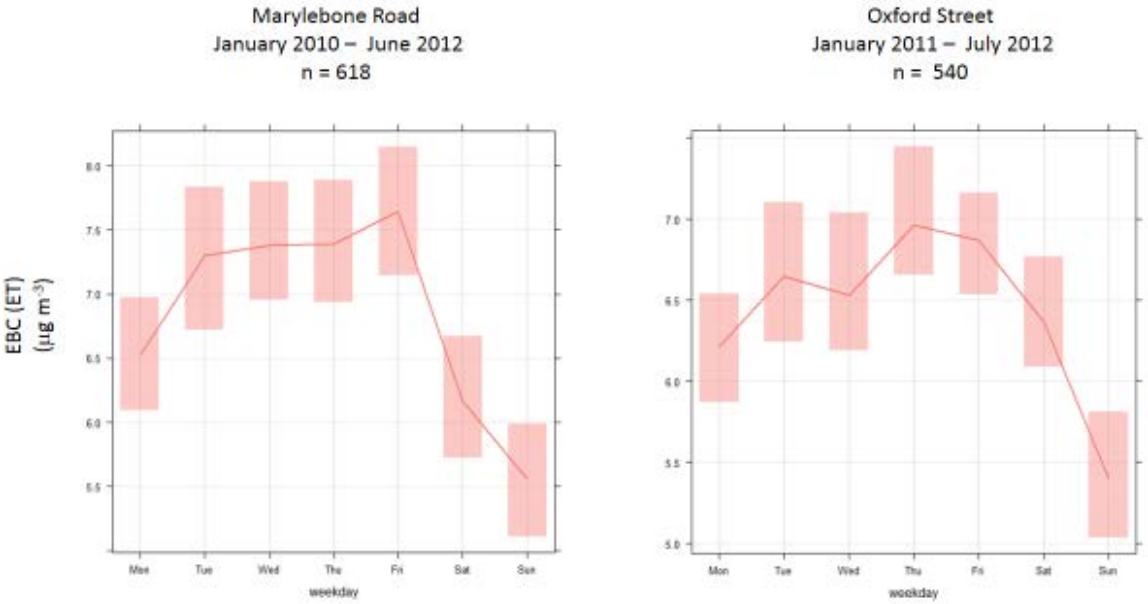
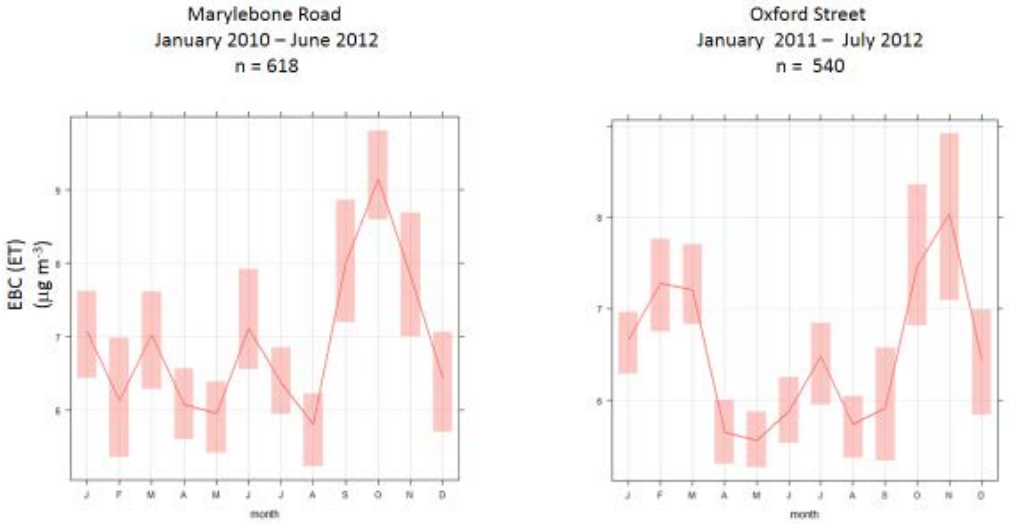



*Figure 6 29. Monthly variation, EBC (ET) (μg m$^{-3}$) Marylebone Road 2010 – 2012, Oxford Street, 2011 - 2012*



## Day of the week variation in traffic flow concentrations and NOx

The day of the week variation in EBC concentrations reported above suggests that human activity is influencing all of these concentrations but there is no indication as to whether this is largely influenced by variation in local traffic flows and type of vehicle. Daily traffic flow data are available for Marylebone Road since 1999 and have been analysed as set out in chapter 2 (i.e. only vehicles falling within the classifications most likely to contain mainly commercial vehicles have been considered). Figures 6.30 and 6.31 are the results of averaging by the day of week in respect of these vehicle categories. As may be seen there was a very distinctive weekday/weekend variation in these vehicle categories suggesting that variation in commercial traffic is a major influence on EBC concentrations at these London sites. Unfortunately changes in the vehicle classification systems discussed in chapter 2 prevent an effective evaluation of how the influence of commercial traffic on these concentrations may have changed over time.

It was established in chapter 5 that there was a strong relationship between EBC concentrations and NOx concentrations (ppb) (with a range of r values between 0.84 and 0.95) determined at Marylebone Road and Acton Town Hall. NOx concentrations at these sites have therefore also been analysed for day of the week variation – see Figures 6.32, 6.33 and 6.34. Only days where collocated EBC concentrations were available have been used to ensure that the analysis days are the same. The day of week variation in NOx supports the variation ascertained in the EBC concentrations at each site with less noticeable reductions in weekend concentrations at Acton Town Hall when compared with Marylebone Road. This may well be due to commercial traffic having less influence on concentrations at Acton Town Hall.

*Figure 6.30 Day of the week variation in numbers s of vehicles in CLS 4 and CLS 5 1999 – 2010 (n = 3466), Marylebone Road – see chapter 2 for explanation of classification system*

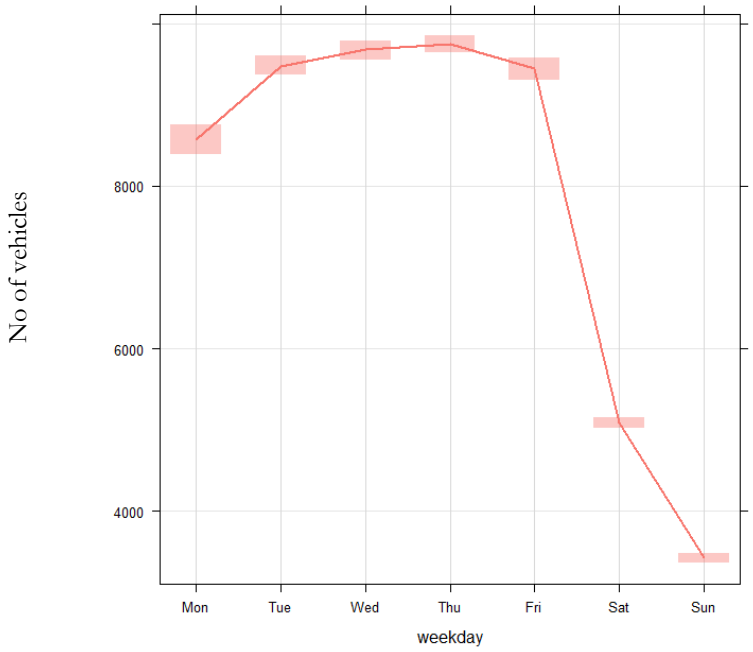



*Figure 6.31 Day of the week variation in numbers of vehicles in CLS 0 and CLS 9 January 2007 – March 2012 (n = 1728), Marylebone Road – see chapter 2 for explanation of classification system*

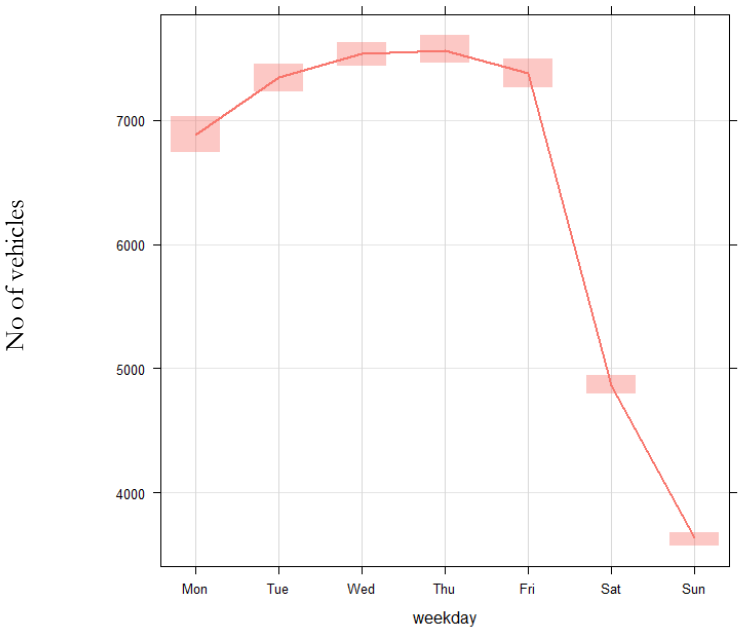


*Figure 6.32 Day of week variation in NOx (ppb) concentrations, Acton Town Hall 2001 – 2002*

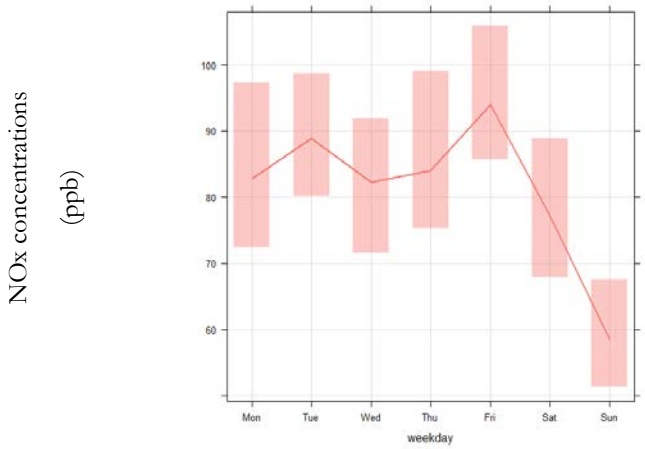



*Figure 6.33 Day of week variation in NOx (ppb) concentrations, Marylebone Road 2003 - 2005*

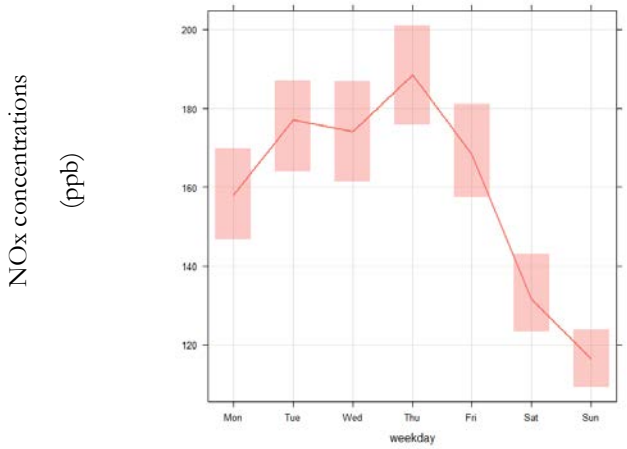
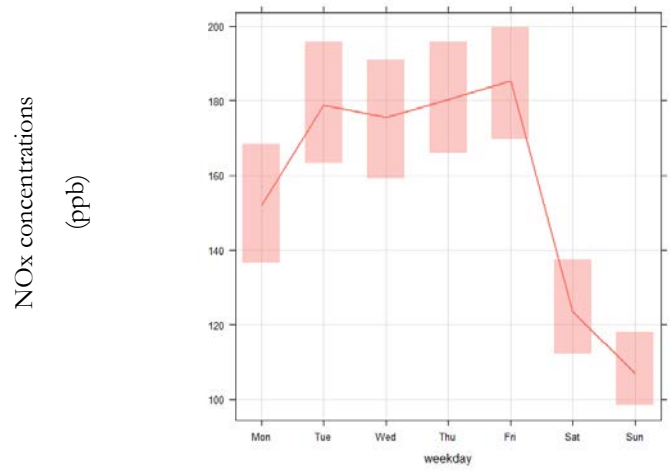



*Figure 6.34 Day of week variation in NOx (ppb) concentrations, Marylebone Road 2009 - 2012*



# EBC concentrations grouped by $PM_{10}$ concentrations

As in chapters 3 and 4, daily PM10 mass concentrations were grouped into bins of mean 10 μg $m^{-3}$ concentrations of PM10. The mean (arithmetic) EBC concentrations, determined using the equations derived in chapter 5 and reported above, have then been calculated for each bin. Only EBC concentrations based on transmissometer measurements from Partisol filters are discussed here. The same procedure has not been adopted for the EBC (BS) concentrations determined for Marylebone Road and Greenwich High Road, based on the Black Smoke (British) measurements, reported above as they have not been derived directly from filter measurements.

The results of this analysis are shown in Figures 6.35– 6.39 and mean concentration details are set out in Table 6.6. Percentage contributions to PM10 mass concentrations are also included. It is worth noting that as a result of using different equations calibrated against the same method of EC measurement (NIOSH-TOT) for the different filter substrates, the influence, or otherwise, of the filter substrate is no longer relevant when comparing results across time (although the PM10 'bins' may be different).

Between 2001 and 2005 at Acton Town Hall, North Kensington and Marylebone Road (Figures 6.35 – 6.37) there was a clear increase in EBC concentrations as PM10 mass increases such that EBC concentrations were almost a magnitude greater on the highest pollution days compared with days when PM10 mass concentrations were less than 20 μg $m^{-3}$ at each site.

The concentrations at each type of location were also distinctive between 2001 and 2005. At the urban background site at North Kensington the highest number of days fell within the <20 μg $m^{-3}$ PM10 mass concentration bin (n = 45) and mean EBC concentrations were in the region of 1.0 μg $m^{-3}$. At the roadside suburban site at Acton Town Hall the highest number of days fell within the 20 – 30 μg $m^{-3}$ PM10 mass concentration bin (n = 108) and mean EBC concentrations were in the region of 1.8 μg $m^{-3}$, almost twice those experienced on the majority of days at the background site. At Marylebone Road, a central London kerbside site, the majority of days occurred when PM10 mass concentrations were in the 30 – 40 μg $m^{-3}$ range and mean EBC concentrations were in the region of 6.8 μg $m^{-3}$, approximately seven times higher than the majority of days at the urban background site and three times higher than the suburban roadside location.

*Table 6.6 mean EBC (QT and ET) concentrations grouped by 10 μg $m^{-3}$ increments in PM10 concentrations at each sampling location 2001 - 2012*

| **Site Sampling period** | **<20 (95% C.I.)** | **20 – 30 (95% C.I.)** | **30 – 40 (95% C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95% C.I.)** | **>60 (95% C.I.)** |
|---|---|---|---|---|---|---|
| | EBC (QT) (μg $m^{-3}$) | | | | | |
| Acton Town Hall January 2001 – December 2002 | 1.3 (1.1,1.4) | 1.8 (1.6,2.0) | 3.2 (2.8,3.6) | 4.1 (3.3,4.9) | 5.3 (4.2,6.5) | 7.3 (3.3,11.4) |
| %age contribution to PM10 concentration | 8% | 7% | 9% | 9% | 10% | 10% |
| No of sample days | 60 | 108 | 58 | 24 | 17 | 6 |
| North Kensington 2003 – 2005 | 1.0 (0.7,1.3) | 1.1 (0.9,1.3) | 1.4 (1.1,1.8) | 3.2 (1.4,5.0) | 6.0 (0, 13.3) | - |
| %age contribution to PM10 concentration | 6% | 5% | 4% | 7% | 9% | |
| No of sample days | 45 | 41 | 17 | 7 | 5 | - |
| Marylebone Road 2003 - 2005 | 1.7 (1.2,2.2) | 3.7 (3.1,4.2) | 6.8 (6.0,7.5) | 8.8 (7.9,10.7) | 9.2 (7.7,10.7) | 11.0 (9.3,12.6) |
| %age contribution to PM10 concentration | 11% | 15% | 19% | 20% | 17% | 15% |
| No of sample days | 5 | 29 | 45 | 42 | 17 | 19 |
| | EBC (ET) (μg $m^{-3}$) | | | | | |
| Marylebone Road January 2010 - June 2012 | 3.6 (3.3,3.9) | 5.7 (5.5,6.0) | 7.7 (7.5,8.0) | 8.6 (8.1,9.0) | 10.0 (9.2,10.8) | 8.0 (7.1,9.0) |
| %age contribution to PM10 concentration | 23% | 23% | 22% | 20% | 18% | 12% |
| No of sample days | 89 | 171 | 210 | 81 | 40 | 23 |
| Oxford Street January 2011 – July 2012 | 4.9 (4.6,5.2) | 5.9 (5.7,6.1) | 7.1 (6.9,7.4) | 8.1 (7.5,8.6) | 7.6 (6.2,9.0) | 8.2 (7.4,9.0) |
| %age contribution to PM10 concentration | 29% | 24% | 21% | 19% | 14% | 11% |
| No of sample days | 71 | 246 | 136 | 45 | 16 | 26 |

*Figure 6.35 mean EBC (QT) concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentrations at Acton Town Hall, 2001 – 2002*

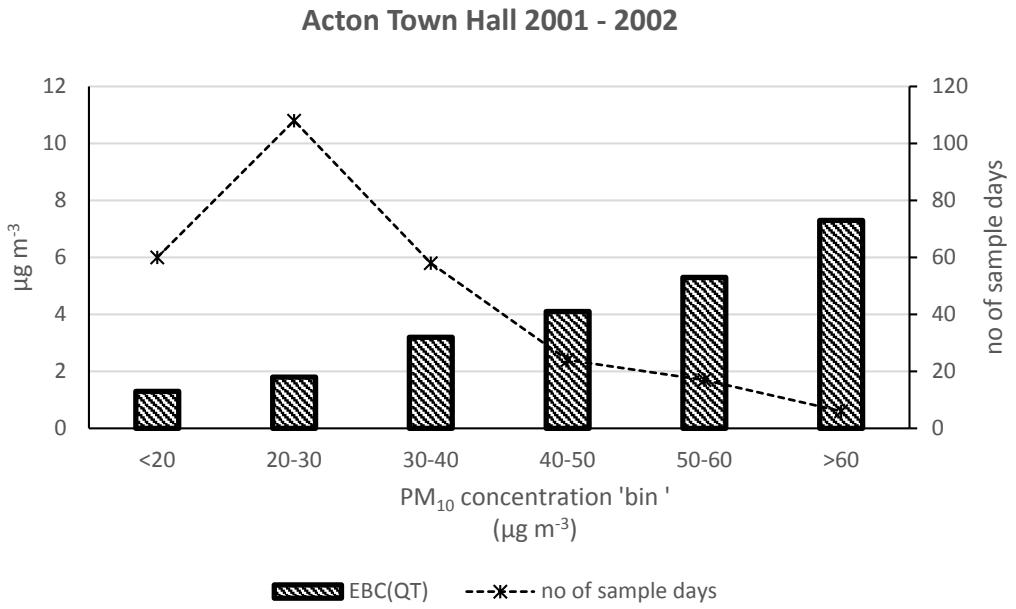



*Figure 6.36 mean EBC (QT) concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentrations at North Kensington, 2003 - 2005*

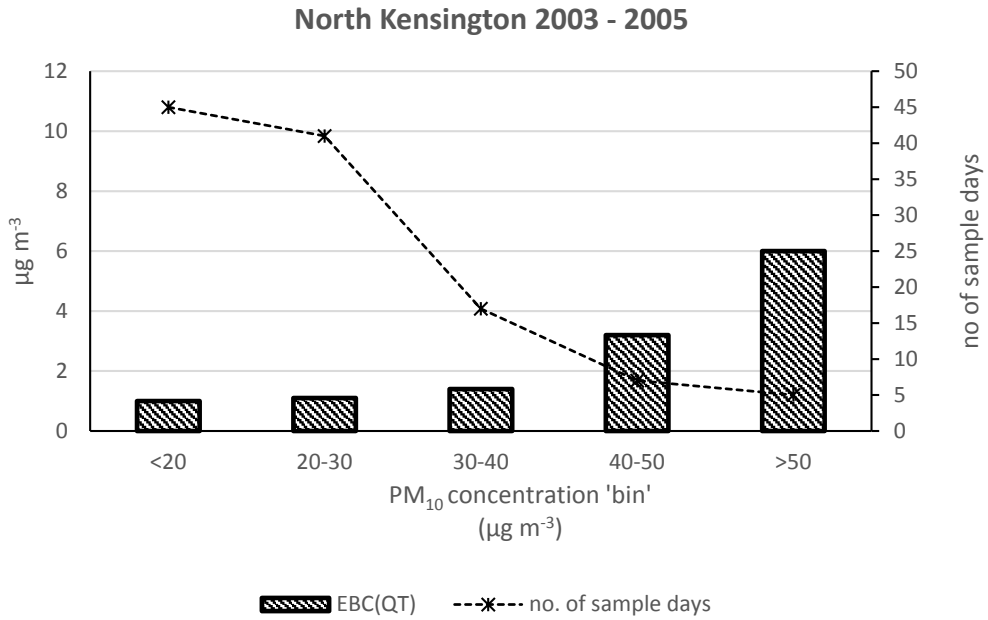
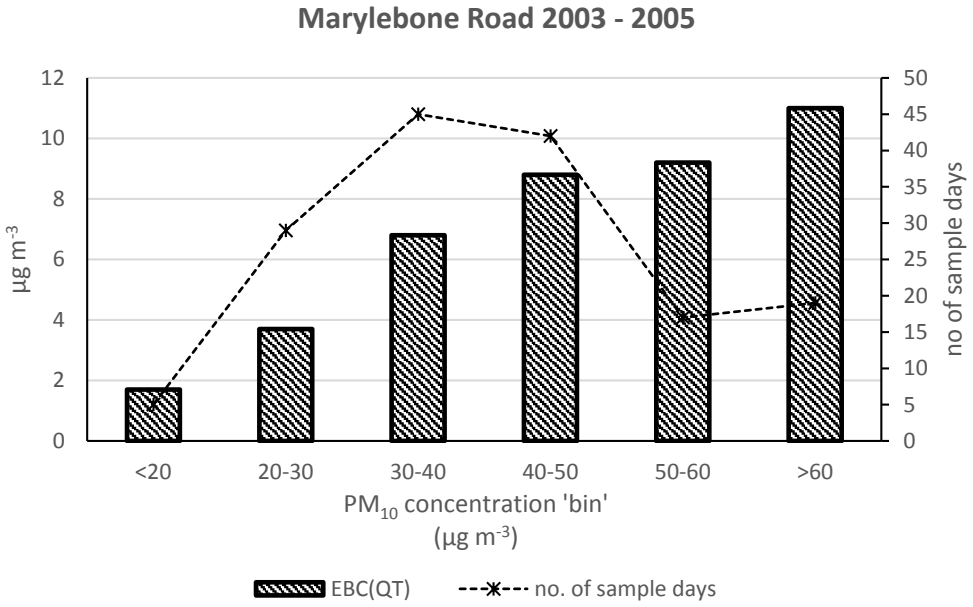


*Figure 6.37 mean EBC (QT) concentrations grouped by 10 μg m$^{-3}$ increments in PM10 concentrations at Marylebone Road 2003 - 2005*



At Marylebone Road between 2010 and 2012 (Figure 6.38 ) when PM10 mass concentrations are between 30 and 60 μg $m^{-3}$ mean EBC concentrations reveal no changes to the corresponding concentrations measured at Marylebone Road between 2003 and 2005 (Figure 6.37). There was a possible reduction in EBC concentrations on days when PM10 mass concentration was more than 60 μg $m^{-3}$ but this may be as a result of a smaller sample size. What is interesting is that EBC concentrations at lower PM10 mass concentrations were higher than the comparative bins for 2003 – 2005. Therefore the difference between high pollution days and other days is less noticeable. Additionally the majority of days occurred within the same PM10 mass concentration bin (30 – 40) but the mean EBC concentration between 2010 and 2012 was higher by approximately 20% (6.3:7.7). Therefore more of the population were exposed to higher concentrations of EBC on more days at Marylebone Road in 2010 – 2012 compared to 2003 – 2005.

The same day EC concentrations determined by the NIOSH-TOT method at North Kensington have been included in Figure 6.38 to demonstrate the difference between concentrations at an urban background site and the roadside increment in EBC concentrations at Marylebone Road. This roadside increment is set out in Table 6.7, and as may be seen never comprised less than 70% (and generally more than 80%) of total EBC concentrations measured at the site.

*Table 6.7 EBC (ET) roadside increment (μg $m^{-3}$) Marylebone Road 2010 – 2012 grouped by 10 μg $m^{-3}$ increments in PM10 mass concentrations*

| **Sampling period Site** | **<20 (95% C.I.)** | **20 – 30 (95% C.I)** | **30 – 40 (95% C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95% C.I.)** | **>60 (95% C.I.)** |
|---|---|---|---|---|---|---|
| | EBC (ET) (μg $m^{-3}$) | | | | | |
| No of sample days | 89 | 171 | 210 | 81 | 40 | 23 |
| January 2010 - June 2012 Marylebone Road | 3.6 (3.3,3.9) | 5.7 (5.5,6.0) | 7.7 (7.5,8.0) | 8.6 (8.1,9.0) | 10.0 (9.2,10.8) | 8.0 (7.1,9.0) |
| North Kensington | 0.7 (0.6,0.8) | 0.9 (0.8,0.93) | 1.0 (0.9,1.1) | 1.5 (1.3,1.7) | 2.0 (1.5,2.4) | 2.4 (1.7,3.2) |
| roadside increment Marylebone Road | 2.9 (80%) | 4.8 (84%) | 6.7 (87%) | 7.1 83%) | 8.0 (80%) | 5.6 (70%) |

Higher mean EBC concentrations at lower PM10 mass concentrations were also notable at Oxford Street (Figure 6.39). Between 20 and 50 μg $m^{-3}$ PM10 mass concentrations, EBC(ET) concentrations at both Oxford Street and Marylebone Road were very similar during the study periods. However, below 20 μg $m^{-3}$ PM10 mass concentrations, the mean EBC concentrations at Oxford Street were higher. This is particularly noticeable when considering the roadside increments set out in Table 6.8 for Oxford Street. The percentage roadside increment at Oxford Street was higher than Marylebone Road with a range between 74% and 90%.

*Table 6.8 EBC (ET) roadside increment (μg $m^{-3}$) Oxford Street 2011 – 2012 grouped by 10 μg $m^{-3}$ increments in PM10 concentrations at Oxford Street*

| **Sampling period Site** | **<20 (95% C.I)** | **20 – 30 (95% C.I.)** | **30 – 40 (95% C.I.)** | **40 – 50 (95% C.I.)** | **50 – 60 (95% C.I.)** | **>60 (95% C.I.)** |
|---|---|---|---|---|---|---|
| | EBC (ET) (μg $m^{-3}$) | | | | | |
| No of sample days | 71 | 246 | 136 | 45 | 16 | 26 |
| January 2011 – July 2012 Oxford Street | 4.9 (4.6,5.2) | 5.9 (5.7,6.1) | 7.1 (6.9,7.4) | 8.1 (7.5,8.6) | 7.6 (6.2,9.0) | 8.2 (7.4,9.0) |
| North Kensington | 0.5 (0.4,0.6) | 0.75 (0.7,0.8) | 1.1 (1.0,1.2) | 1.6 (1.3,2.0) | 2.0 (1.1,2.9) | 1.8 (1.5,2.0) |
| roadside increment Oxford Street | 4.4 (90%) | 5.2 (88%) | 6.0 (85%) | 6.5 (80%) | 5.6 (74%) | 6.4 (78%) |

*Figure 6.38 Marylebone Road EBC(ET) in PM10 2010 – 2012, and same day North Kensington EC (NIOSH- TOT), grouped by 10 μg m$^{-3}$ increments in PM10 concentrations at Marylebone Road*

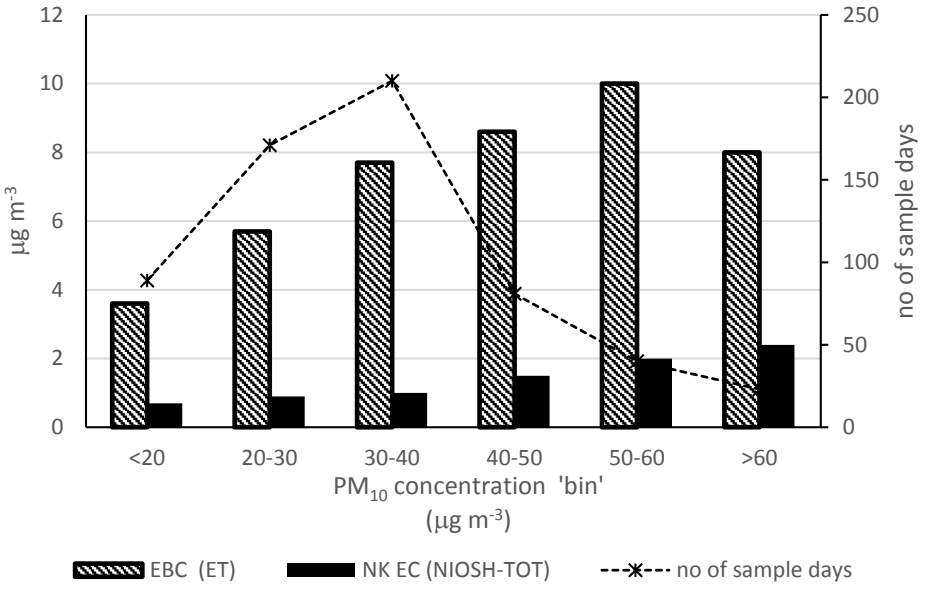
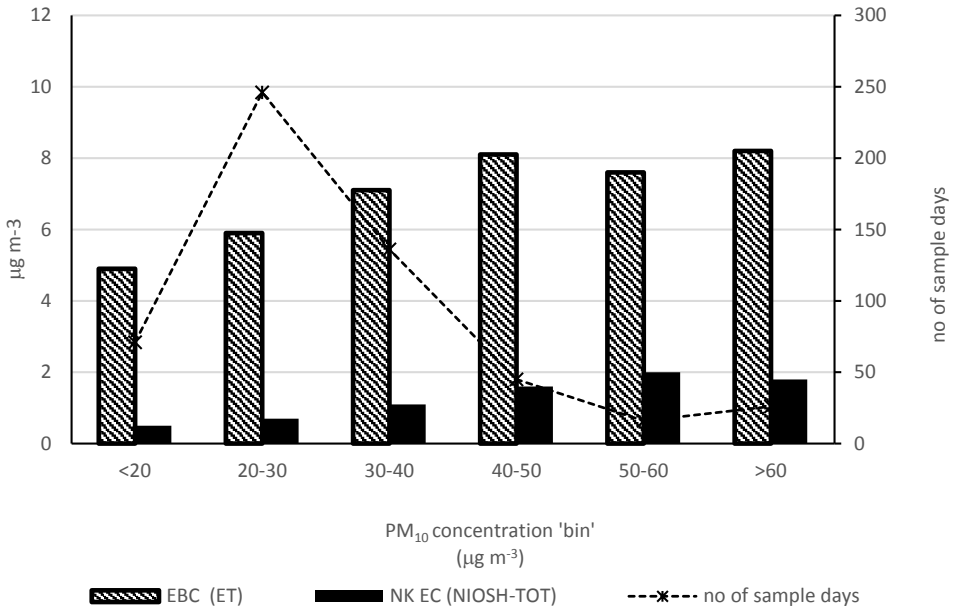
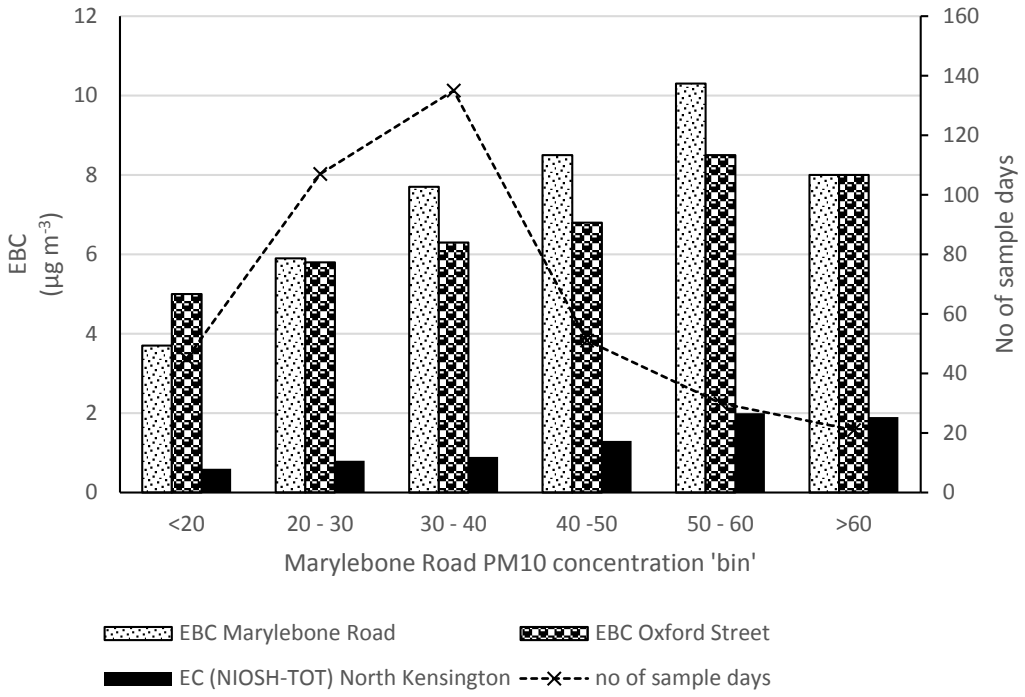



*Figure 6.39 Oxford Street EBC (ET) in PM10 2010 – 2012, and same day North Kensington EC (NIOSH TOT), grouped by 10 μg m$^{-3}$ increments in PM10 concentrations at Oxford Street*



Same day EBC(ET) concentrations were compared between Marylebone Road and Oxford Street grouped according to PM10 mass concentrations at Marylebone Road and are shown in Figure 6.40 (North Kensington EC measurements have also been added). At the lowest and highest PM10 concentration 'bins' there was no difference between EBC concentrations at the two sites. EBC concentrations were higher at Marylebone Road on days when PM10 concentrations (at that location) were between 30 and 60 μg $m^{-3}$. Nevertheless it is clear that EBC concentrations are high at both locations and making substantial contributions to overall PM10 concentrations.

*Figure 6.40 Same day mean EBC (ET) concentrations (μg $m^{-3}$), Marylebone Road and Oxford Street and EC (NIOSH-TOT) at North Kensington, based on mean PM10 concentration 'bins' at Marylebone Road 2011 – 2012*



# Summary

Black smoke data were collected for many years in the UK and only finished in 2009 following the introduction of the UK Black Carbon Network. Black Smoke measurements from Marylebone Road and Greenwich High Road in south-east London have been converted to equivalent black carbon measurements using the equation provided by Heal and Quincey (2012). At Greenwich High Road there was a significant downward trend in concentrations between 1990 and 2008 but this trend was not apparent in the black smoke data at Marylebone Road for the period 1999 to 2009. Trend analysis was more difficult at Marylebone Road because of gaps in the data between 2002 and 2006. There was however a drop in mean concentration of EBC during this period in the region of 11%. Trend analysis carried out after 2006 showed no discernible trend however. Day of week variation was noticeable at both sites with lower concentrations apparent on Sundays. Seasonal differences at Greenwich High Road, with lower concentrations in the summer months, were noticeable but not mirrored at Marylebone Road.

The lack of any trend in concentrations of EBC at Marylebone Road was also noticeable in concentrations between 2003 and 2005 and 2010 and 2012, calculated using the transmissometer method developed in this study. During 2003 and 2005 no significant trend in concentrations was noticeable at Acton Town Hall but there was a small downward trend ($p < 0.05$) at North Kensington. The situation is different at Oxford Street during 2011 to 2012 where there was a significant ($p < 0.01$) upward trend suggesting that concentrations had risen by at least 11% during this short period. This should, however, be treated with some caution as buses were on diversion away from Oxford Street at the beginning of 2011 and may have suppressed EBC concentrations during this period. This would require further investigation before any conclusions may be drawn but there is no apparent indication of any reduction in these concentrations.

Daily and seasonal analysis revealed lower concentrations on Sundays but highest concentrations of EBC occurred during the autumn months at all sites except Marylebone Road between 2003 and 2005, but it was noticeable at that site during the period 2010 to 2012. This in contrast to the anion measurements reported in chapter 4.

Grouping the mean EBC concentrations revealed that there was a distinctive hierarchy between the sites with the lowest concentrations at the urban background site. The concentrations were higher at Acton Town Hall and highest at Marylebone Road and Oxford Street. Concentrations at these two central London locations were very similar. There would also appear to be less variation between concentrations of EBC as PM10 mass concentrations increased suggesting that seeking compliance with regulatory requirements and dealing only with days when the Daily Limit Value is exceeded would not bring about a reduction in EBC concentrations.

As the vehicles using Oxford Street are all diesel-powered there can be no doubt that this type of vehicle is making an increasingly important contribution to PM10 concentrations in Oxford Street. Additionally the percentage of total EBC concentrations which may be regarded as a roadside increment (by deducting the amount of EC measured at North Kensington) is higher in Oxford Street than Marylebone Road and on most days is in the region of 90% of total EBC concentrations.

In conclusion, the use of a method based on the light absorption properties of archived filters has been demonstrated to provide key information about concentrations of EBC at various sites, including at an important location where measurements would otherwise be unavailable (Oxford Street).

# Chapter 7

# General Discussion and Conclusions

The analysis carried out in the previous chapters considered concentrations of PM10 and its main components by considering each component separately. Discussion of the results for each component and subsequent analysis were included in each chapter. In this chapter the analysis carried out in the previous chapters is drawn together and appraised in the context of the objectives and research aims set out in chapter 1.

## Research Objectives

The first objective of this research was to compile datasets of PM and its key components at different locations in London for the period 2001 - 2012. Data from urban background, roadside, and kerbside monitoring sites would be expected to represent a range of exposure locations in London. Measurements of the concentrations of PM10, PM2.5, sulphate, nitrate, chloride together with equivalent black carbon would further be expected to provide information about secondary, natural and primary sources of PM.

In 2001 to 2002 a field sampling campaign using a Partisol 2025 dichotomous sampler was carried out at Acton Town Hall a roadside site in west London. These were one of the first UK urban measurements of the contribution made by anions, elemental carbon and organic carbon to PM10 mass concentrations. There was also a novel separation of the fine and coarse PM size fractions. The dataset remains the only comprehensive interpretation of PM10 mass concentrations at an urban roadside site in outer London. It therefore provided a unique base from which to assess change.

Publicly available datasets of PM concentrations at North Kensington, an urban background site, Marylebone Road, a kerbside site, and Oxford Street, also a kerbside site, in London (2002 – 2012) were utilised. Gravimetric measurements obtained from Partisol 2025 samplers were available and were chosen to provide continuity with the measurements made at Acton Town Hall as well as enabling interpretation of data from archived filters collected by this method. As discussed in chapter 2, choice of sampler site is a compromise but the trafficked sites in this study have a number of features in common, such as their west-east orientation, making comparison between them more effective. In addition, also as discussed in chapter 2, the uncertainty associated with each measurement method remains similar by the choice of using the same sampling method for comparison. 95% confidence intervals have been calculated to provide a measure of the range of uncertainty throughout this thesis.

A comprehensive dataset of anion concentrations (sulphate, nitrate and chloride) on PM filters collected using a Partisol 2025 since 2002 at both North Kensington and Marylebone Road was combined with the anion measurements from Acton Town Hall to provide the opportunity for consistent analysis of the contribution made by inorganic sources. No separate cation measurements were made and these anion concentrations were converted to ammonium sulphate, ammonium nitrate and sodium chloride as described in chapter 2.

Black carbon or elemental carbon are important key indicators of primary sources of vehicle tailpipe emissions from diesel fuelled vehicles in $PM_{10}$ but are difficult to assess over the study period using only publicly available data because of changes in monitoring methods. Therefore a method for determining equivalent black carbon concentrations from archived gravimetric filter samples was developed as part of this study (Objective 2). Light absorbing carbon on archived quartz fibre and Emfab$^{TM}$ filters collected by Partisol 2025 samplers at Acton Town Hall, Marylebone Road, North Kensington and Oxford Street was measured by both reflectometry and transmissometry.

This is one of the first studies to compare reflectometry and transmissometry results directly from the same filter and to report measurements by either method using Emfab$^{TM}$ filters. There was a strong relationship between the two measurement methods

but there also appeared to be substrate dependencies of the physical properties of black carbon on different filters. It is likely that the way in which particles become embedded on different filter substrate determines their apparent physical properties because of potential interaction with the substrate. Filter substrate was therefore deemed to be an important consideration and each filter type considered separately.

Relationships between the transmissometer and reflectometer measurements and available collocated elemental carbon concentrations ($\mu g\ m^{-3}$) were determined empirically using filters collected at Acton Town Hall, Marylebone Road and North Kensington (no elemental carbon measurements were available from filters collected at Oxford Street).

The measurement of light absorption by a particular species (in this case particulate carbon) using either reflectometry or transmissometry would be expected, in accordance with Beer-Lambert Law, to be capable of being described by a straight line linear regression relationship. However, in line with other studies (e.g. Weingartner et al., 2003, and Lack et al., 2014), this was found not to be the case when considering filters loaded with particulate matter. This lack of linear response was attributed to the effects of light scattering by other particles on the filter as well as possible shadowing and is referred to as a loading or shadowing effect (see for example Virkkula et al, 2007). In each case the relationship was best described empirically by a quadratic equation ($r^2$ between 0.65 and 0.95) and four separate equations were determined (Equations 5.7, 5.9, 5.11, and 5.13). Following the method set out by Heal and Quincey (2012) a range of both mass extinction coefficients ($\sigma ATN$) ($m^2\ g^{-1}$) and loading correction factors *(k)* were determined based on these equations (Table 5.5). Both $\sigma ATN$ and *k* determined by this method differed by filter substrate type and method of measuring light absorption. These results highlighted the difficulties of seeking to determine a simple generic mass extinction coefficient in relation to particulate carbon on PM filters. Furthermore, simply basing mass extinction coefficients and loading factors on relationships determined in a quadratic equation is not sufficient to define the physical processes that describe light absorption by black carbon when collected as part of a particle ensemble on filters. However, this conclusion does not affect the results of this study as the empirically determined relationships could be used to calculate equivalent black carbon concentrations.

Equivalent black carbon concentrations were first determined using all four equations and compared both to each other and to collocated NOx measurements. To determine equivalent black carbon measurements (EBC) for comparison in this study, it was decided to use the separate equations derived using the transmissometer measurements for quartz fibre filters and Emfab™ filters as follows:

$$\textbf{Quartz filters: EBC}(\mu g\ m^{-3}) = 0.8605\ \left(ln\ (\frac{Io}{I})^2\right) + 0.7382\ \left(ln\left(\frac{Io}{I}\right)\right)$$

**(Equation 5.9 )**

$$\textbf{Emfab}^{TM}\textbf{ filters EBC}\ (\mu g\ m^{-3}) = 0.359\ \left(ln(\frac{Io}{I})^2\right) + 4.8311\ \left(ln\left(\frac{Io}{I}\right)\right)$$

**(Equation 5.13 )**

$$Where\ \ \ln\left(\frac{Io}{I}\right) = \frac{\frac{transmissometer}{ATN}}{100}$$

The basis for this decision was that there was no need to compensate for any possible additional reflectance of light back through the filter as only one beam of light was transmitted at a specific wavelength known to be a better indicator of light absorbing black carbon. In addition the empirically determined quadratic equations were based on a comparison with the same elemental carbon measurement method (TOT).

The equations were used to determine EBC concentrations at

- Acton Town Hall, 2001 – 2002, (quartz)
- Marylebone Road and North Kensington, 2003 – 2005 (quartz)
- Marylebone Road, 2010 – 2012 (Emfab™) and
- Oxford Street 2011 – 2012 (Emfab™).

These measurements provided a unique record of black carbon concentrations both before 2007 when details of equivalent black carbon concentrations in London were sparse and at sites where routine black carbon measurements were not otherwise available.

A summary and timeline of the datasets compiled for analysis in this study are set out in Table 7.1. In addition black smoke data converted to black carbon collected at Marylebone Road and Greenwich High Road were utilised in chapter 6.

*Table 7.1 Summary and timeline of datasets used for analysis throughout study*

| Species | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $PM_{10}$ | Acton Town Hall | | | | | | | | | | | |
| | | Marylebone Road | | | | | | | | | | |
| | | North Kensington | | | | | | | | | | |
| | | | | | | | | | | | Oxford Street | |
| $PM_{2.5}$ | Acton Town Hall | | | | | | | | | | | |
| | | Marylebone Road | | | | | | | | | | |
| | | North Kensington | | | | | | | | | | |
| ammonium sulphate | Acton Town Hall | | | | | | | | | | | |
| | | Marylebone Road | | | | | | | | | | |
| | | North Kensington | | | | | | | | | | |
| ammonium nitrate | Acton Town Hall | | | | | | | | | | | |
| | | Marylebone Road | | | | | | | | | | |
| | | North Kensington | | | | | | | | | | |
| sodium chloride | Acton Town Hall | | | | | | | | | | | |
| | | Marylebone Road | | | | | | | | | | |
| | | North Kensington | | | | | | | | | | |
| EBC | Acton Town Hall | | | | | | | | | | | |
| | | | Marylebone Road | | | | | | | Marylebone Road | | |
| | | | North Kensington | | | | | | | | | |
| | | | | | | | | | | | Oxford Street | |
| EC (TOT) | | | | | | | | | | North Kensington | | |

The datasets were systematically evaluated to consider and compare differences and similarities in concentrations (objective 3). Each species was considered separately starting with overall PM10 and PM2.5 concentrations and the methods of analysis used were consistent. An innovative method used in this study was to 'bin' the species under consideration by 10μg $m^{-3}$ increments of PM10 concentrations providing a different perspective to other air quality studies (e.g. Harrison et al., 2004, Yin and Harrison, 2008) regarding the way in which the contribution of different species changed at different concentrations of PM. The behaviour of each species has been discussed in detail in each of the relevant chapters (3.4 and 6).

# Research Aims

Utilising the analysis carried out to achieve the stated objectives, it is possible to consider the two research aims which have underpinned this research project, namely understanding

- whether there have been any changes in concentrations of each species between 2001 - 2012, including high pollution days, and
- the impact of air quality initiatives introduced in London between 2001 and 2012 (as set out and discussed in chapter 1).

## Variation in the composition of $PM_{10}$ and its components (2001 - 2012)

There were clear differences in weekday to weekend concentrations of both $PM_{10}$ and $PM_{2.5}$ at all sites indicating local primary sources on mass concentrations were important, particularly at the roadside sites. $PM_{2.5}$ was the principal component of PM concentrations on high pollution days, considered to be those days when $PM_{10}$ concentrations were above 50 $\mu g\ m^{-3}$, at all sites excluding Marylebone Road. At this site the coarse fraction made a significant contribution even on high pollution days. Trend analysis revealed that there was an upward trend in both $PM_{10}$ and $PM_{2.5}$ concentrations before 2006. The change of filter substrate from quartz fibre to Emfab™ in 2007 because of possible artefacts linked to the quartz fibre filter (Maggs et al., 2008) altered the apparent frequency of high pollution days and confounded an effective assessment of the influence of policies to control emissions. Looking separately at measurements using each substrate, there is no evidence that $PM_{10}$ or $PM_{2.5}$ concentrations have decreased at the study sites between 2001 and 2012.

Filter substrate is not a relevant consideration when considering the anion concentrations as the species are removed from the filter in solution before being analysed and therefore are comparable over the study period. In addition, by using the different calibrations for quartz fibre and Emfab™ filters determined in this study to calculate EBC concentrations those concentrations are also comparable over the study period, although no EBC concentrations were determined in respect of filters from North Kensington after 2009.

Figure 7.1 compares the mean (arithmetic) concentrations of ammonium nitrate and ammonium sulphate before 2005 at Acton Town Hall, Marylebone Road and North Kensington and after 2010 at Marylebone Road and North Kensington. Mean concentrations of EBC are compared between Acton Town Hall, Marylebone Road and North Kensington before 2005 and after 2010 at Marylebone Road. Details and 95% CIs are set out in Table 7.2. Sodium chloride has not been included as there were no changes in concentrations of this species during the study period.

Overall there has been little change in the total of the combined (mean) contribution made by the three species studied in Figure 7.1 to PM10 concentrations but some individual differences are discernible.

There was a reduction of ammonium sulphate concentrations in the region of 12% at both Marylebone Road and North Kensington. Whilst interpretation of these reductions is not straightforward, investigation in this study supports the view suggested by Jones et al. (2011) that they occurred at the time of the introduction of ultra-low sulphur fuel in the UK. A comparison of weekday/weekend concentrations also suggested that there was a link between local emissions and ammonium sulphate concentrations. It would seem that road traffic emissions make an important contribution from local traffic sources to ammonium sulphate concentrations. This conclusion contrasts with the evidence of only a modest UK urban increment from sulphate above the rural background (see for example Abdalmogith and Harrison, 2006, Yin and Harrison, 2008) and the accepted view that sulphate concentrations are determined by more distant regional sources. Given that only the UK introduced ultra-low sulphur fuel at the end of 2007, it may be concluded that UK emissions have an important influence on measurements of sulphate in the UK. Further trend analysis on data collected after 2009 shows a small upward trend. This may be as a result of increases in more regional sources, such as electricity generation in the Thames Estuary to the east of London, shipping or an increase in the proportion of diesel vehicles in the UK fleet.

A reduction of mean EBC concentrations in the region of 7% was identifiable at Marylebone Road after 2010 but this reduction was outweighed by a 12% increase in mean ammonium nitrate. In addition mean ammonium nitrate increased by 5% at North Kensington.

*Figure 7.1 Comparison of mean concentrations (μg m $^{-3}$) of EBC, ammonium nitrate and ammonium sulphate at Acton Town Hall, Marylebone Road and North Kensington 2001 - 2012*

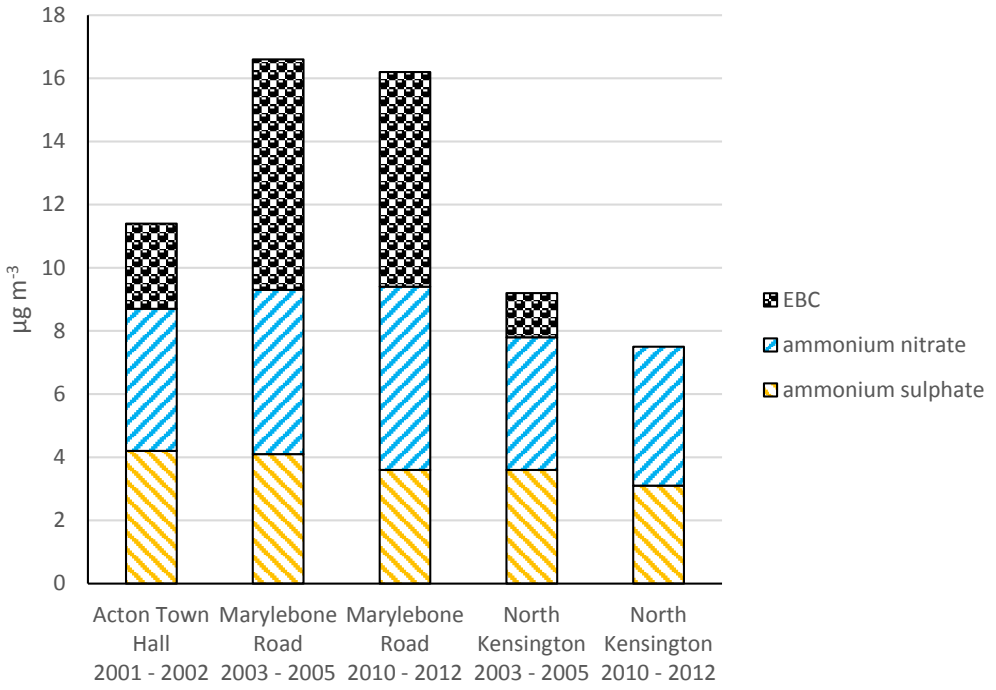



*Table 7.2 Mean concentrations (μg m $^{-3}$) of EBC, ammonium nitrate and ammonium sulphate at Acton Town Hall, Marylebone Road and North Kensington 2001 – 2012*

| Site | Sampling period | EBC (95%CIs) | Ammonium nitrate (95%CIs) | Ammonium sulphate (95%CIs) |
|---|---|---|---|---|
| | | (μg m$^{-3}$) | | |
| Acton Town Hall | 2001 - 2002 | 2.7 (2.4,2.9) | 4.5 (4.1,4.9) | 4.2 (3.9,4.4) |
| Marylebone Road | 2003 – 2005 | 7.3 (6.8,7.9) | 5.2 (4.1,6.3) | 4.1 (3.7,4.6) |
| | 2010 - 2012 | 6.8 (6.6,7.0) | 5.8 (5.2,6.5) | 3.6 (3.3,3.8) |
| North Kensington | 2003 – 2005 | 1.4 (1.1,1.8) | 4.2 (3.4,5.0) | 3.6 (3.2,4.0) |
| | 2010 - 2012 | N/A | 4.4 (4.0,4.8) | 3.1 (3.0,3.3) |

The contribution to overall PM10 and, in particular, high pollution days by all components is however dependent on the PM monitoring method (since it defines the high pollution days) and filter substrate. This is discussed in more detail in the next section.

## High pollution days

In order to implement effective policies based on the underlying monitoring method, it is important to understand the changes in the distribution of the species measured in this study to overall PM10 concentrations and particularly changes of composition on high pollution days as a result of the filter change. This change of perspective could lead to different management options for high pollution days. High pollution days in this study are considered to be those where the Daily Limit Value has been exceeded.

Table 7.3 summarises the percentage contributions which each measured component in this study has been found to contribute to PM10 concentrations sampled on different filter substrates at each location both on days when PM10 concentrations are below and above 50 μg $m^{-3}$ (i.e. the Daily Limit Value).

*Table 7.3* *Summary percentage contribution made by each measured component to PM10 concentrations in London, 2001 – 2012*

| | | ammonium sulphate | | ammonium nitrate | | sodium chloride | | EBC | |
|---|---|---|---|---|---|---|---|---|---|
| | | <50** | >50*** | <50** | >50*** | <50** | >50*** | <50** | >50*** |
| | | QUARTZ FIBRE FILTER | | | | | | | |
| Acton Town Hall | 2001 - 2002 | 13% | 15% | 13% | 21% | 6% | 1% | 6% | 9% |
| North Kensington | 2002 - 2006 | 15% | 16% | 15% | 23% | 8% | 4% | 3% | 7% |
| Marylebone Road | 2002 – 2006 | 10% | 11% | 10% | 15% | 7% | 5% | 17% | 15% |
| | | EMFAB™ FILTER | | | | | | | |
| North Kensington | 2009 – 2012 | 17% | 11% | 21% | 38% | 11% | 3% | 3% | 3% |
| Marylebone Road | 2009 – 2012 | 9% | 11% | 12% | 25% | 7% | 5% | 22% | 16% |
| Oxford Street | 2011 - 2012 | - | - | - | - | - | - | 23% | 12% |

<50** mean PM10 mass concentration less than 50 μg $m^{-3}$

>50*** mean PM10 mass concentration more than 50 μg $m^{-3}$ ("high pollution day")

Anion concentrations at different PM10 concentrations as a consequence of filter substrate changes for PM10 monitoring have not previously been reported. The most noticeable changes were between ammonium nitrate concentrations particularly on days above the EU daily limit value as identified by the gravimetric measurements. Prior to 2006 ammonium nitrate contributed 15% to PM10 mass concentrations (quartz fibre filter substrate) on episode days at Marylebone Road and 23% at North Kensington which was similar to measurements reported by Yin and Harrison (2008) who made an adjustment for particle bound water which was not made in this study. However, when considering high pollution days after 2009 ammonium nitrate contributed 25% at Marylebone Road and 38% at North Kensington to overall PM10 mass concentrations.

As discussed in chapters 1 and 4, increased concentrations of secondary inorganic species and in particular ammonium nitrate may be linked to the availability of ammonia from agricultural practices particularly in the spring months. After 2009, at Marylebone Road 33 of the 75 days (44%) and at North Kensington 17 of the 46 days (37%) when the daily limit value was exceeded occurred in the months of March and April. Considering only those days where PM10 concentrations were greater than 60 μg $m^{-3}$ at Marylebone Road, 20 out of 33 days (more than 60%) occurred in these months. There would therefore seem to be strong evidence supporting the linkage between agricultural practices and breaches of the daily limit value.

The percentage contribution made by ammonium sulphate to high pollution days remained similar to days when the daily limit value was not exceeded before 2006 and this continued to be the case at Marylebone Road after 2009. However, the percentage contributions changed at North Kensington after 2009. The percentage contribution made by ammonium sulphate changed from 17% when the daily limit value was not exceeded to 11% when it was exceeded, suggesting its influence on urban background concentrations has become less significant on high pollution days possibly as a result of the introduction of ultra-low sulphur fuel.

In contrast to ammonium nitrate, the percentage contribution made by sodium chloride generally went down on high pollution days but an examination of the contribution made by chloride in the fine fraction at Acton Town Hall suggests that there are times when concentrations of chloride are influential on high pollution days. This was particularly noticeable at Acton Town Hall at the beginning of November when fireworks may have made a higher contribution to particulate chloride than sea-salt. This may have important

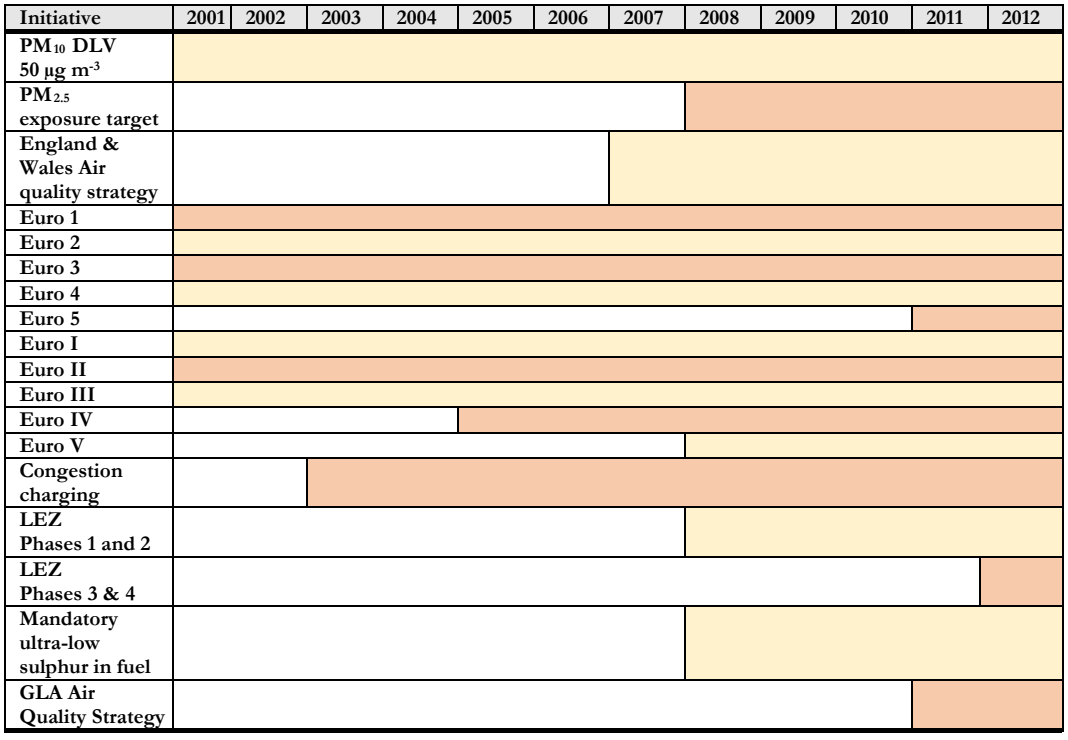
policy implications as currently chloride measurements are used to determine the contribution made by sea-salt which may be discounted for regulatory compliance purposes based on an annual mean concentration of chloride. However, as demonstrated in chapter 4 the overall mean concentration of chloride does not alter on high pollution days but the distribution between chloride in the fine and coarse fractions reverses suggesting that anthropogenic chloride is more influential on high pollution days. Coupled with the re-distribution of mass measurements associated with the filter change discussed above it is suggested that the current model for assessing the sea-salt component needs to be re-visited.

Between 2003 and 2005, on days when PM10 concentrations were less than 50 μg $m^{-3}$ at North Kensington, Acton Town Hall and Marylebone Road the percentage contribution made by EBC concentrations to PM10 mass concentrations was 3% at North Kensington, 6% at Acton Town Hall and 17% at Marylebone Road. On high pollution days this hierarchy remained with 7% at North Kensington, 9% at Acton Town Hall and 15% at Marylebone Road. These results contrast with those of Yin and Harrison (2008) who found at sites in Birmingham that the percentage contribution made by EC (measured by thermal optical transmission (TOT) method) dropped from 8% on all days to 4.9% on episode days between 2004 and 2006. Between 2010 and 2012 however percentage contributions at Marylebone Road changed, most probably as a result of the filter change from quartz to Emfab™. On days when the daily limit was not exceeded EBC contributed 22% to PM10 concentrations at Marylebone Road and 23% at Oxford Street. It is important to note therefore that nearly a quarter of PM10 concentrations comprised EBC on the majority of days at these central London sites compared to 3% at the urban background location (North Kensington) emphasising the importance of introducing policies to control emissions of EBC on all days. This would necessitate a different focus than concentrating simply on reducing the number of days when the daily limit value is exceeded. On high pollution days 16% of PM10 mass concentrations was EBC at Marylebone Road whilst at Oxford Street it was 12%.

## Impact of relevant air quality initiatives in London, 2001 - 2012

A summary and timeline of the various initiatives which may influence air quality in London as discussed in chapter 1 is set out in Figure 7.2. By looking at the initiatives in this way it is apparent that most of the various strategies have been introduced since 2008 and many of them have been phased introductions making it potentially difficult to establish "before and after" effects. However, none of the strategies have been abandoned and therefore it might be hoped that there would be a cumulative effect of the various initiatives.

*Figure 7.2* *Timeline of initiatives potentially impacting/improving air quality in London in relation to ambient PM10, 2001 – 2012*




These strategies (other than the congestion charging scheme) have been introduced to reduce ambient air pollutants and the primary aim has been to improve health outcomes in the general public.

Ammonium sulphate has demonstrated a noticeable reduction during the study period and this coincides with the introduction of ultra-low sulphur fuel for vehicles. At least one of the initiatives has therefore apparently been successful. However, there are also signs that ammonium sulphate concentrations have started to rise again suggesting that other sources, either regional or an increase in the proportion of diesel-fuelled vehicles in the fleet, are becoming increasingly important in controlling these concentrations.

It is more difficult to assess the success of the other initiatives. The lack of any progress in reducing particulate nitrate is almost certainly linked to two factors. Agricultural and land management practices contributed to springtime episodes in particulate nitrate and coupled with the failure of the EURO standards to abate NOx emissions from diesel sources as reported by Carslaw et al., (2011) have led to an overall increased contribution by ammonium nitrate to PM10.

Current (2014) strategies place the greatest emphasis on reducing the number of days when the daily limit value is exceeded to enable compliance with regulatory standards. The research carried out in this project makes it clear that the most efficacious strategy to reduce the number of days when the daily limit value was exceeded in London and achieve compliance would be to seek the reduction of ammonium nitrate concentrations. However, as discussed in chapter 1 there is less compelling evidence that adverse health effects are associated with concentrations of secondary inorganic particles such as ambient ammonium nitrate (see for example Kelly and Fussell, 2012). Focussing solely on high pollution days in London would fail to reduce pollutants which may have the most significant adverse health effects but do not make the greatest contribution to high pollution days, e.g. EBC. The analysis throughout this study has demonstrated that concentrations of EBC do not change in line with PM10 concentrations. Any comparison of health exposure studies needs to take into account these differing perspectives.

In this study EBC concentrations have been considered in detail as the best indicator in trends in tailpipe emissions and modest reductions have been detected at North Kensington and Marylebone Road. At two sites, Oxford Street and Greenwich High Road, there were significant trends but in different directions. There seemed to be an apparent and significant rise in EBC concentrations at Oxford Street without a commensurate trend in PM mass concentrations. At the start of 2011 (and hence at the start of the analysis carried out in relation to Oxford Street) buses were on diversion from Oxford Street due to Crossrail ( a new west-east railway line for London) works taking

place at Tottenham Court Road (www.tfl.gov.uk). It may be that the EBC concentrations from buses were suppressed at the start of the study period at Oxford Street and the concentrations recorded after October 2011 are a better interpretation of EBC concentrations at this site. Effective trend analysis is not possible over the remaining time period in this study but there would not seem to be any reductions in EBC concentrations during the study period at this location. The lack of change in overall PM mass concentrations at the beginning of 2011 may be due to a balancing rise in the coarse fraction from the nearby construction works. At Greenwich High Road there seemed to be a very abrupt drop in EBC concentrations (based on black smoke measurements) at the end of 1999. It is difficult to be certain of the cause of this change without further investigation but it coincides with the opening of the Docklands Light Railway extension to Greenwich and Lewisham. It may be an indication of changes in choice of transport mode to and from work combined with the completion of the construction works. The results from considering EBC concentrations at Oxford Street, where EBC concentrations were lower at the start of 2011, and Greenwich High Road, where EBC concentrations were demonstrably lower after 1999, suggest that reductions achieved by traffic management measures might bring about long term reductions in tailpipe emissions.

The overall thrust and emphasis of recent strategies as outlined in Figure 7.2 target vehicle tailpipe emissions in London and the results of this research study strongly supports that this emphasis is an important way forward but needs to form part of a range of initiatives. The reductions in ammonium sulphate following the introduction of ultra-low sulphur in fuel demonstrate that effective changes can be introduced.

## Possible future strategies in London

As described in chapter 2, the twenty-three bus routes which use Oxford Street are operated by seven different bus companies. Journey times for each bus to pass through Oxford Street are long (22 minutes). Lord Adonis, the shadow infrastructure Minister, described Oxford Street as a "barely moving glacier of red metal" in a recent (21 February 2014) article in "The Independent". Transport for London (TfL) through a separate company, London Buses, has responsibility for setting the routes and frequency of buses using London's roads and this is then managed by the separate bus companies. A single bus operator with ownership in the public domain in London might achieve better rationalisation of bus operations and could ensure that all profits be used for inward investment achieving a more rapid improvement in the fleet to minimise emissions. Reductions in EBC concentrations may be achieved more rapidly and efficiently thereby providing a public health benefit to Londoners. There may, as a result, also be reductions in $NO_2$ emissions which are not discussed in any detail in this thesis but are also frequently in excess of regulatory limits in London.

In line with the recommendation of the World Health Organisation (WHO, 2013) there is a need to introduce a limit value/guideline for black carbon, which could be introduced first in large conurbations such as London, as soon as possible and would be particularly useful in determining the effectiveness of any initiatives targeting this species. Such a metric should be based on measurements from roadside sites contrasted with background sites to determine a roadside increment but requires further investigation before appropriate metrics could be introduced.

There is also an urgent need to understand other emissions of PM associated with vehicle use such as road abrasion and brake and tyre wear. The increasing importance of the coarse fraction to PM concentrations at Marylebone Road reported in chapter 3 may well be an indication of the growing importance of this source to local emissions.

Public awareness regarding the adverse health outcomes from poor air quality and the causes is continually being developed and new technology such as smart phones, computer tablets, etc. are at the forefront of this campaign. However, car ownership in the UK is the lowest per capita in London and, whilst decisions made by individuals about choice of transport mode in London and how to avoid pollution hotspots are important, it is emissions from commercial and public transport which need to be targeted. Choices made by the public are important in this process and there is a need to raise awareness in this regard.

The importance of secondary inorganic sources also needs to be highlighted. The springtime episodes of ammonium nitrate emissions noted in this research and elsewhere are a significant factor in the failure to meet the regulatory targets to reduce days when the PM daily limit value of 50 $\mu g\ m^{-3}$ is exceeded in London and these may be linked to emissions of ammonia from agricultural land management practices. There are few sources of this type within the Greater London boundary and therefore London specific initiatives will not be able to make any real impact. Any new initiatives would need to be at the EU and national government level.

## Conclusions

Whilst comprehensive datasets have been collected and analysed, it was not possible to accumulate consistently similar data across the whole timescale because of changes in monitoring methods, in particular a change of filter substrate from quartz fibre to Emfab™ for monitoring purposes. Nevertheless this research has provided fresh insights into the composition of PM10 in London between 2001 and 2012 at typical urban locations providing a sound comparative basis for future analysis of this nature and making an important contribution to understanding air quality in London.

**Key findings** include:

- No evidence of any noticeable reduction in overall PM10 concentrations was found at any of the study sites and the contribution of the coarse fraction seemed to be increasing at Marylebone Road suggesting that other emissions associated with traffic such as road abrasion and brake and tyre wear were becoming increasingly important.
- The daily limit value continued to be exceeded at all the study sites. Springtime episodes were noticeable and seemed to be mainly associated with increased ammonium nitrate concentrations which in turn have been associated with increased availability of ammonia from land management practices.
- Reductions in ammonia sulphate concentrations were identified and associated with the introduction of ultra-low sulphur fuel in the UK indicating that local sources of sulphate may be more important to PM10 concentrations than previously thought.
- All chloride concentrations may not be associated with sea-salt and a proportion may be from anthropogenic sources, particularly on high pollution days.
- The change of filter substrate mentioned above resulted in a redistribution of concentrations of ammonium nitrate, ammonium sulphate and sodium chloride in overall PM10 concentrations. This re-apportionment based on Emfab™ filters highlights important differences to previous studies based on quartz fibre filters (e.g. AQEG 2012) and needs to be incorporated into assessments of the composition of PM10 and associated abatement strategies.

- EBC concentrations are capable of being determined based on either transmissometry or reflectometry measurements although filter substrate is an important consideration. Important differences between filter substrates (quartz fibre and Emfab$^{TM}$) were identified and linked to different multiple light scattering properties of the particles collected on, and potentially within, the different filter substrates.
- A number of important insights into EBC concentrations over time were made including at sites where concentrations would not otherwise be available (e.g. Oxford Street). The contribution made by EBC concentrations were important to overall PM10 concentrations on all days and not just when considering days when the daily limit value had been exceeded. This is an important consideration for health studies and further emphasises the need for a separate limit value/guideline for EBC concentrations.
- Some health studies utilise the calculation provided in ISO 9835 (1993) to determine an absorption coefficient (*a*) (see, for example, Eeftens et al., 2012) as a surrogate for equivalent black carbon. This calculation is however dependent on the underlying filter substrate which does not seem to be taken into account in these health studies. A more sensitive interpretation would be to use EBC concentrations based on the method developed in this research.
- Modest reductions in EBC concentrations after 2010 may be linked to the introduction of new initiatives in London although the absence of a longer timeframe of measurements makes this difficult to confirm with any confidence.
- Archived filters are an important resource for carrying out retrospective analysis and need to be stored with care.

# Some recommendations for future research

The new equations determined in this study provide an opportunity to build a retrospective EBC time series utilising archived filters, including at sites where only PM10 concentrations are currently available, which may be used in both health and source policy studies. This research could further be used to determine why EBC concentrations are not going down significantly despite progressively stringent EURO classes and address the question of whether abatement policy has failed or has been balanced by increasing use of diesel-fuelled vehicles. It may also indicate whether there is a need to reappraise the emphasis on policies promoting the use of diesel fuelled vehicles in Europe and be of use in any proposal to introduce a new limit value/guideline for EBC as proposed by the World Health Organisation (2013).

Continuing research of EBC concentrations at Oxford Street may also address the specific questions about the impact of progressive improvements in emissions for TfL controlled fleets (buses and taxis).

More transmissometry measurements of different filter types would continue to provide insights into the behaviour of particles once collected on a filter substrate and in particular the influence of the loading or shadowing effect of the particles. Other conceptual frameworks determining loading and shadowing factors could be explored in future work (see for example Gundel et al., 1984). This research would also be relevant when considering correction factors for the 'real-time' measurements of EBC provided by Aethalometers or other similar monitoring methods.

Other emissions associated with vehicles, such as road abrasion and brake and tyre wear, are currently overlooked and there are no planned initiatives specifically to control these emissions. However, it would seem that the coarse fraction, where these sources are most likely to make a contribution, is increasing at trafficked sites such as Marylebone Road. A method for quantifying these sources is becoming increasingly important. Possible future work to isolate these traffic related sources could potentially use the relationship between the derived EBC concentrations, NOx concentrations and PM10 concentrations similar to the model developed by Fuller et al., (2002) which identified primary sources in PM10 based on the relationship with NOx emissions. The use of other data such as vehicle flows might also be utilised for this purpose.

Springtime peaks in $PM_{10}$ and $PM_{2.5}$ concentrations identified at North Kensington and Marylebone Road in this study seemed to be mainly associated with increased ammonium nitrate concentrations which in turn have been associated with increased availability of ammonia from land management practices. More research is needed to confirm this association.

Reductions in ammonium sulphate concentrations at the time of the introduction of ultra-low sulphur fuel in the UK (and only in the UK at that time) were identified in this study suggesting a roadside contribution to this species. However most studies apportion ammonium sulphate in the UK to mainly regional sources. Further research is needed to determine a UK traffic contribution to secondary sources.

Finally, investigations in this study suggest that the influence of anthropogenic chloride on high pollution days requires further investigation particularly in the context of apportioning all measured chloride concentrations to natural (sea-salt) sources.

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